Few-photon coherent nonlinear optics with a single molecule

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The pioneering experiments in linear spectroscopy were performed using flames in the 1800s, but nonlinear optical measurements had to wait until lasers became available in the twentieth century. Because the nonlinear cross-section of materials is very small12, macroscopic bulk samples and pulsed lasers are usually used. Numerous efforts have explored coherent nonlinear signal generation from individual nanoparticles5–8 or small atomic ensembles9–11 with millions of atoms. Experiments on a single semiconductor quantum dot have also been reported, albeit with a very small yield. Here, we report the coherent nonlinear spectroscopy of a single molecule under continuous-wave single-pass illumination and the switching of a laser beam by on the order of ten pump photons. The sharp molecular transitions and efficient photon-molecule coupling at a tight focus10 allow for optical switching with less than a handful of pump photons and are thus promising for applications in quantum engineering11.

The schematic of our experiment, which was performed in a helium bath cryostat, is depicted in Fig. 1a and described further in the Methods. Two laser beams at frequencies νpmp (pump) and νprb (probe) were incident on a thin naphthalene sample that contained a very small concentration of dibenzanthanthrene (DBATT) molecules. A solid immersion lens (SIL) combined with a simple aspheric lens provided a tight focus for the probe beam with a divergence of ≃20 mrad, whereas the pump beam, which was offset from the lens axis (see Fig. 1a), was spatially filtered out by the collecting aspheric lens. In addition, we used cross-polarized detection to reduce the contribution of the pump to the transmitted probe beam12.

Figure 1b shows the energy level scheme for DBATT. The so-called 0–0 zero-phonon line (00ZPL) with a lifetime-limited linewidth of γ = 20 MHz at the wavelength of λ = 619 nm connects the vibrational ground states of the electronic ground (S0) and excited (S1) states. An important advantage of our system is the large extinction cross-section of about 0.5(3λ2/2π) ≃ 200 nm2,12 where the factor 0.5 signifies that about 50% of the population from the excited state decays via redshifted fluorescence channels.

The interaction of a two-level atom with two optical fields of amplitudes Eνpmp and Eνprb at frequencies νpmp and νprb has been described in several works8–10,12,13. The bichromatic excitation can be expressed as a nonlinear-modulated field, resulting in a time-dependent Rabi frequency Ω(t) modulated at frequency δ = 2νprb − νpmp (ref. 8). Using a Fourier ansatz for the Bloch vector gives:

\[ \rho_{01}(t) = \sum_{n=0}^{n_{max}} (u_n + i v_n) e^{i2\Omega(t)\tau + \delta} \]

where \( \rho_{01} \) denotes the off-diagonal element of the density matrix decomposed in the nth harmonic orders of the Bloch vector components \( u_n \) and \( v_n \). The appearance of the harmonics of δ in equation (1) indicates a nonlinear process and exchange of energy between the two beams. In an alternative picture (Fig. 2g,h), the pump field ‘dresses’ the molecular levels, giving rise to new transitions at \( \nu_{pfb} = \nu_{pmp} \pm \Omega_pmp \) with the pump-generalized Rabi frequency defined as \( \Omega_pmp = \sqrt{\Omega_pmp^2 + \Delta^2} \). Here Ωpmp is the Rabi frequency caused by the pump and \( \Delta = \nu_{pmp} - \nu_{mol} \) denotes the detuning between the pump frequency and the molecular resonance.

We start by examining the transmission spectra of the probe laser beam under different pump intensities and frequency detunings. Comparison of the spectra in Fig. 2a,b recorded in the absence of the pump beam with the data in Fig. 2c,d measured at Ωpmp < I reveals that even at such low intensities, there is a clear redistribution of energy between the pump and the probe. These features become even more pronounced for more intense pump beams. Figure 2e,f illustrates an example for a value of Ωpmp just under 2I. The solid red lines in Fig. 2 display numerical fits (see Methods).

To provide an intuitive understanding of the multiphoton processes involved, in Fig. 2g,h we plot the dressed energy levels for the data recorded at pump detunings of 0 MHz (left column) and 5 MHz (right column), respectively. We note, however, that contrary to the usual usage of the dressed-state picture under strong illumination, Ωpmp in our measurements remains of the order of I. Consequently, the observed features are less obviously attributable to well-defined transitions among the dressed states but result from the coherent addition of contributions from various channels.

The symmetric sidebands in Fig. 2e are the precursors of the Mollow triplet, where a strong driving field creates sidebands in the atomic fluorescence spectrum spaced by the Rabi frequency13. In an extinction measurement such as that taken here, the sidebands become dispersive and are spaced by ±Ωpmp9,12,14. A comparison of the data in the left and right columns shows that a frequency detuning of the pump beam (here from 0 to 5 MHz) results in an asymmetry between the blue- and red-detuned spectral features. We have introduced a colour coding to relate the spectral features of Fig. 2e,f to the different pump and probe scattering processes denoted in Fig. 2g,h. Each colour group consists of different channels involving the pump (solid line) and probe (dashed line). The grey and black arrows indicate the strength of the transition based on the populations of the states involved, which in turn depend on Δ.

In the region of \( \nu_{pfb} \approx \nu_{pmp} + \Omega_pmp \) highlighted in blue, a three-photon process occurs where two pump photons are absorbed and one probe photon is emitted in a stimulated process. In this case, the molecule ends up in the excited state S1 and returns to the ground state after a spontaneous decay. The resulting fluorescence signal was used to detect this hyper-Raman phenomenon on a single
DBATT molecule for a large $\Delta$ (ref. 18). Here, we have provided direct evidence for the coherent amplification of the probe beam by a single molecule and for a very small $\Delta$. The red region in Fig. 2f can be interpreted as the a.c. Stark shift of the extinction dip (see Fig. 2b) detuned by about $\Omega_{\text{pmp}}$. In this case, the weight of the corresponding three-photon process is negligible. The dispersive feature marked in green represents stimulated Rayleigh scattering around $\nu_{\text{p}} \sim \nu_{\text{pmp}}$, a coherent process that involves energy transfer between the pump and the probe $^7, ^{19}$.

The interaction of the molecule and the pump photons can not only modify the transmitted probe beam, but can also produce light at other frequencies $^2$. To investigate this effect, we used a time-correlated single-photon counting system in a start–stop configuration (see Methods) and searched for the beating of the probe beam with any other

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**Figure 1** | Experimental set-up. **a**, Schematics of the optical arrangement in the cryostat operating at 1.5 K. **b**, The energy level scheme of a DBATT molecule (see text and Methods for details).

**Figure 2** | Resonant and near-resonant pump-probe spectroscopy. **a**, **b**, Transmitted power of a weak probe beam as its frequency is scanned across the resonance of a single molecule in the absence of a pump beam. **c**, **e**, Same as in **a** but in the presence of a resonant pump beam at two different strengths. **d**, **f**, Same as in **b** but in the presence of a pump beam at $\Delta = 5$ MHz at two different strengths. The Rabi frequency noted on the lower right corner of each figure gives a measure of the pump intensity. The zeros on the horizontal axes indicate the pump frequency (denoted by the vertical dashed lines). The vertical blue lines show the resonance frequency of the unperturbed molecule in each case. The solid red lines are numerical fits using the orders $n = -10$ to $+10$ in equation (1). **g**, **h**, The dressed states of the molecule and the different excitation paths for $\Delta = 0$ (**g**) and $\Delta = 5$ MHz (**h**). The dashed and solid arrows depict the probe and pump photons, respectively. The thicker and thinner levels in **h** signify the asymmetric distribution of populations. Similarly, the black and grey arrows represent more and less probable transitions, respectively, in each case.
signal. We then calculated the Fourier transform of the recorded time-dependent measurement for each pump–probe detuning \( \delta \). Figure 3a shows the outcome for a measurement at \( \Delta = 18 \) MHz. The most dominant feature in this figure appearing at frequency \( \delta \) is marked (i) and stems from the interference of the probe beam with the residual amount of pump light. In addition, however, the data points labelled (ii) reveal the existence of a beating signal at \( 2\delta \). Figure 3b sketches the four-wave mixing process involving a degenerate pump beam and a new signal \( \nu_{\text{WMM}} \) at frequency \( \nu_{\text{p}} - 2\delta \) (ref. 16). The strength of this signal is about 3% of that at \( \delta \), and it disappears when the pump and probe lasers are detuned away from the molecular resonance.

So far we have addressed the steady-state interaction between the pump and probe beams as mediated by the molecule in frequency space. To visualize the dynamic temporal behavior described in equation (1) directly, we used the time-dependent measurement described above to monitor the population of the excited state by recording the fluorescence signal. To achieve a strong modulation of the excited state population and a large beating visibility, we set \( \Omega_{\text{p}} = \Omega_{\text{pmp}} = 140 \) MHz. As illustrated in Fig. 4a, we expect the fluorescence to drop when destructive interference reduces the total electric field to zero. When the field builds up again, the molecular emission undergoes Rabi oscillations that are damped by the spontaneous emission to a steady-state level.

Figure 4b–d displays three time-resolved fluorescence signals, where \( \Delta \) was kept at zero and \( \delta \) was varied. In Fig. 4b, the Rabi frequency quickly reaches significant values within a time frame much shorter than the fluorescence lifetime \( T = 1/2\nu_{\text{f}} \), allowing for Rabi oscillations to be observed. In both cases, the variation of \( \Omega(t) \) with time causes a chirp in the temporal oscillations equivalent to subharmonic Rabi resonances in the frequency domain.

In Fig. 4d, the excited-state population is not changed for most of the beating period because the driving field saturates the molecule within a time comparable to \( T \), reducing the visibility of Rabi oscillations. We remark in passing that due to the extremely low power involved and the very high quantum efficiency of the molecules, one need not worry about heating artefacts in our system.

Our measurements show that the sharp Fourier-limited ZPL of a single molecule can efficiently couple photons at two or more frequencies. Such nonlinear interactions are of great interest in the context of quantum information processing, where single quanta of light and matter would be used to transport or mediate information. A key step in many of these endeavours is to switch an optical field with only a few photons, or ideally one. We now show that our system readily enters this regime. Let us start with the green transmission spectrum in Fig. 5a, where a single molecule attenuates a detected light signal by 30% (see Methods for details). The blue spectrum in Fig. 5a shows that we can recover the transmitted signal at \( \nu_{\text{mol}} \) if we turn on a pump field with \( \Omega_{\text{pmp}} = 50 \) MHz and \( \Delta = 18 \) MHz. To assess the switching quality, we define \( T_{\text{on}}/T_{\text{off}} \) as the switching contrast, where \( T_{\text{on}} \) and \( T_{\text{off}} \) denote the transmitted probe power with the pump on and off, respectively. As displayed by the red curve in Fig. 5a, we reach a switching contrast of about 1.8 dB.

In our current sample, the molecules required 6–30 incident photons within an excited-state lifetime to scatter one photon (see Methods). However, theory predicts that this coupling can reach 100% in the case of perfect mode matching and a unity fluorescence branching ratio. Figure 5b displays an example of high switching performance if we consider a probe beam with \( \Omega_{\text{p}} = 1/4 \), choose \( \Delta = 1/2 \) and set \( \Omega_{\text{pmp}} = 1.5\nu_{\text{f}} \). This regime corresponds to a saturation parameter \( S_{\text{pmp}} = \Omega_{\text{pmp}}^{2}(2\Delta^{2} + \Gamma^{2}/4) \sim 2 \), implying that a pump field with less than a handful of photons per pulse can efficiently switch a beam of light (see Methods).

Following the advent of single-molecule spectroscopy, several groups have also reported on nonlinear studies of single molecules. However, these efforts have mostly detected the incoherent fluorescence signal and have not been concerned with optimizing the nonlinear yield. In this work, we have demonstrated the coherent nonlinear interaction of a single organic molecule with a very weak nearly-resonant narrow-band field. Given the simplicity of our approach, it can also be readily applied to other quantum systems that have a high degree of coherence such as atoms in vacuum, rare-earth ions in crystals or semiconductor...
quantum dots. The intrinsically efficient nonlinear cross-sections of such two-level-like quantum systems can be further improved by combining a tight focusing arrangement with broadband sub-\(\lambda^3\) microcavities, paving the way for single-photon switching.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

A.M. and B.G. performed the experiments and analysed the data. V.S. conceived the project. All authors discussed the results. A.M., B.G. and V.S. wrote the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.
Methods

Sample preparation. To reduce the effect of background fluorescence and optimize the focusing ability of the SIL, we fabricated our sample in a shallow channel etched into a fused silica cover glass (220 nm deep and 500 μm wide) that is sealed by the SIL (cubic zirconia). This is done by bringing the SIL and the cover glass into optical contact, where they are drawn together by van der Waals forces. Subsequently, a small piece of solid naphthalene doped with DBATT was placed on the cover glass, next to the SIL and the whole sample was heated by a Peltier element until the naphthalene melted. The liquid naphthalene was drawn into the channel through an opening by capillary forces. The sample crystallized after cooling. The concentration of DBATT molecules corresponded to the observation of one molecule every 20 GHz within one focal spot.

Optical set-up. The two laser beams were generated from the same dye laser with a linewidth of about 2 MHz by using two acousto-optical modulators in a double-pass configuration with variable detuning of ~80 to +130 MHz. By tuning the laser frequency to the resonances of the molecules in the inhomogeneously broadened absorption band of DBATT inside a naphthalene crystal, we could address each individual molecule separately. The transmitted laser intensity as well as the backscattered redshifted fluorescence were measured with single-photon counting modules. The pump and probe Rabi frequencies were determined by measuring the broadening of the 00ZPL in a power-dependent saturation study.

Theoretical model. The interaction of the pump and a two-level system is treated exactly within the usual approximations (only dipole interaction, rotating wave approximation). The probe beam, on the other hand, is treated perturbatively so that higher orders of n are required if ΔRinc is large (as in Fig. 4). However, in the other parts of our work where the probe is weak, the dominant term is n = 1 and the contribution of the n = 2 term can be as small as 1%. We emphasize that even the n = 1 term corresponds to a nonlinear response of the system. In other words, this is not to be associated with a x2 process.

Spectral drift compensation. The investigated nonlinear effects are very sensitive to small frequency variations of only a few MHz. Although DBATT in naphthalene is a very stable system, small spectral drifts remain. To counter these residual slow drifts the transmission signal was measured during a fast sweep of the probe frequency. The spectral position of the molecule was measured and the frequency of the pump beam was adjusted to maintain the desired relative detuning. This procedure was repeated several 100 times until a typical integration time of 1 s per data point was reached.

Time-resolved measurements. To register the temporal development of the signal, we measured the delay between the arrival of a transmitted photon and a reference signal. The latter was extracted from the beating of the pump and probe beams on an avalanche photodiode in front of the cryostat. This was done by using a time-correlated single-photon counting system (HydraHarp, PicoQuant) in a start–stop configuration. To record more than one beating period every fifth stop pulse was taken. The rest of the pulses were sorted out by setting an artificial dead time using a pulse delay generator (Stanford Research DG645).

Spatially filtered detection. For the switching experiment, we spatially selected the transmitted light by a single mode fibre to improve the efficiency of the destructive interference that leads to the extinction signal. In this fashion, we could reach an extinction value of about 30%, and the relative suppression of the pump beam was improved to more than 200. We note that we did not implement this filtering process in other measurements to ensure that the degree of photon–molecule coupling was not masked further.

Coupling efficiency. It is instructive to see what incident photon rate Rinc is required to achieve a photon scattering rate Rscatt. Combining equations (1) and (3) of ref. 10, for steady-state monochromatic excitation, it can be shown that in the case of perfect mode matching,

\[ \frac{R_{\text{scatt}}}{R_{\text{inc}}} = \frac{2\sigma}{\sigma_0} \]

where \( \sigma = (f^2(f^2 + 4\Delta^2))(1/(1 + S))n_0 \) is the scattering cross-section at a given finite incident power and \( S = \Delta^2/(2\Delta^2 + f^2/4) \) denotes the saturation parameter in the general case of detuned excitation. Using these results and the textbook relation \( S = \sigma/2(\Delta + 1) \) from ref. 39, with \( \rho_{ee} \) as the excited state population, we arrive at

\[ R_{\text{scatt}} = \frac{S^2}{2} \left( 1 + \frac{4\Delta^2}{f^2} \right) \]

Following this derivation, we find that an average of 2 incident photons per lifetime is sufficient to reach \( S = 2 \) at \( \Delta = f/2 \) in the ideal case of perfect coupling.

In the sample used in this study, we determined that 6–30 photons per excited-state lifetime (corresponding to an incident power of 240 pW–1.2 nW) can suffice as the average rate of \( R_{\text{inc}} \) at the location of a molecule for reaching \( S = 2 \) on resonance. Here, we carefully calibrated the optical losses through the cryostat windows and lenses on the way to the sample to provide tight focusing. The spread in the measurement stems from the variation in the molecular dipole orientation, fluorescence branching ratio and focusing quality. We note, however, that the measurements presented here were all performed on the same single molecule.

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