



PAPER

Detuning dependent Rabi oscillations of a single molecule

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A single organic dye molecule at cryogenic conditions is resonantly excited in a confocal microscope. Under strong laser illumination it undergoes Rabi oscillations. Mathematically, this was well described and had been experimentally implemented. These oscillations can be measured as side-bands on their resonance fluorescence, e.g. in the Mollow-Triplet. An alternative method is to research this effect by an analysis of the single molecule anti-bunched photon statistics. This has been performed in this work. Here we research on the detuning dependence of this signal—it is experimentally demanding since the utilized laser might drift or single emitters are not necessarily spectrally stable enough, such that the spectrum can be measured indefinitely. We therefore apply a measurement technique in which the photon correlation signal is acquired in detuning dependent steps. This is performed by continuous laser sweeps over the single molecule excitation spectrum. A single recording of the anti-bunched photons takes 20–50 ms. After approx. 1 h of repetitive laser detunings a full anti-bunching curve is reconstructed for each spectral position. An alternative technique with 100 ns laser pulses allows us to acquire a set of comparable data. Our study is derived from a single dibenzanthanthrene molecule with a natural linewidth of $2\pi \times 16$ MHz. It emits under resonant excitation more than 380.000 photons per second. Under spectral detuning, Rabi-oscillations are observed up to $\Omega_{\text{Rabi}} = 2\pi \times 160$ MHz.

1. Introduction

The recording and the manipulation of Rabi oscillations reflects the ability to deliberately control the state of a quantum system. This method of coherent control is a required necessity for coherent spectroscopy schemes such as Ramsey spectroscopy [1], Hahn-echo [2] and more sophisticated pulse schemes such as CPMG [3] and adaptive schemes such as GRAPE [4]. These sequences are well established in nuclear magnetic and electron spin resonance field and constantly extended. The underlying physics is well covered mathematically by the Bloch-equations [5].

Shortly after these developments in the radio- and microwave domain, the techniques were extended to the optical control of quantum systems. This field of coherent optical spectroscopy was expedited with the invention of the laser and the rise of quantum optics in the 1960s. Then, atomic beams and single atoms or ions were researched [6]. Afterwards, optical Rabi oscillations have been observed with trapped ions [7], quantum dots [8, 9], defect centers [10–12] and also very early with single molecules [13–15]. The detuning dependent excitation of single emitters allowed to witness if the treatment as a two-level system is applicable for a single emitter, to implement coherent manipulations, and to deliberately transfer a quantum system to its excited state. Such experiments have been performed with non-optical systems [16, 17], but the detuning dependence was already earlier realized with quantum dots [18, 19].

This paper introduces the underlying math in the next chapter. Thereafter, we introduce a Rabi oscillation experiment on a single molecule. The Rabi oscillations are monitored with the help of a second order correlation function. This proves the emitter's coherence and also the single emitter nature simultaneously. An alternative

long optical pulse mode allows to acquire comparable experimental data faster than before. In both of the latter, we focus on the detuning dependence of the Rabi oscillations, which is experimentally challenging since the recording might suffer experimental drift and fluctuating environments of the single molecule. Fine-grained recordings have so far only been performed on very stable quantum systems, and a single molecule with the introduced techniques is ideally suited for such a measurement.

2. Theory

Single molecules under cryogenic conditions are known to emit highly coherent photons which are suitable for quantum interference experiments [20]. Their coherence also manifests in the recording of the photon statistics which shows coherent oscillations between the ground and excited state—so-called Rabi-oscillations [13]. These occur under high excitation powers and are caused by the coherence of the ground and excited state and their coupling with the external light field. To approach such a situation theoretically in a semi-classical approach, we apply the solution of optical Bloch equations and determine the Rabi frequency of an emitter [21, 22]. The so-called dressed state picture implies that the emitter (described by the Hamiltonian H_M) and external laser modes (H_L) can coherently exchange photons, and form subsequently a coupled system, where the full Hamiltonian is expressed as $H_{ML} = H_M + H_L + V_{ML}$. Here, V_{ML} describes the interaction Hamiltonian. The corresponding coupling strength, known as the Rabi frequency, is studied in this paper.

The molecules eigenbasis is subsequently altered, and the interaction with the light field is described as $\langle \text{mol}^*, N | V_{ML} | \text{mol}^g, N + 1 \rangle$. This implies that the molecule is in the ground state and $N + 1$ photons are in the laser mode, and equivalently, the molecule is in the excited state and the laser mode contains N photons. This energy splitting with the Rabi frequency, Ω_{Rabi} , is reflected in the coherent scattering such as in the Mollow-triplet [14, 23]. Earlier, we have introduced a recording where a single molecule was resonantly excited and the Mollow triplet was recorded alongside with the auto-correlation curve of the Stokes-shifted photons [14].

In this work we research on the detuning dependence of the effective Rabi frequency, Ω_{eff} . It is given as

$$\Omega_{\text{eff}} = \sqrt{\Omega_{\text{Rabi}}^2 + \delta^2}. \quad (1)$$

This implies that the Rabi frequency rises with the detuning. Under large detunings, it increases linearly with δ .

The Rabi-oscillations are measured here in the configuration of an auto-correlation function of the photon stream, which has also been performed for defect centers before [12]. A detected photon on one of the detectors projects the molecule into its ground state. Then, the emitter is excited again, which is monitored by observing the Stokes shifted photons from the molecule. This red-shifted emission is proportional to the excited state population (here named as ρ_{22}), although it is a decay into the manifold of vibrational levels of the electronic ground state. The resulting recording of the auto-correlation function shows a dip in the correlation function at zero time differences since the system can only emit a single photon at a time. This phenomenon is often called ‘anti-bunching’.

To calculate the temporal behavior of the coherent emission of a single emitter requires an ansatz which is known as the Bloch equation as follows:

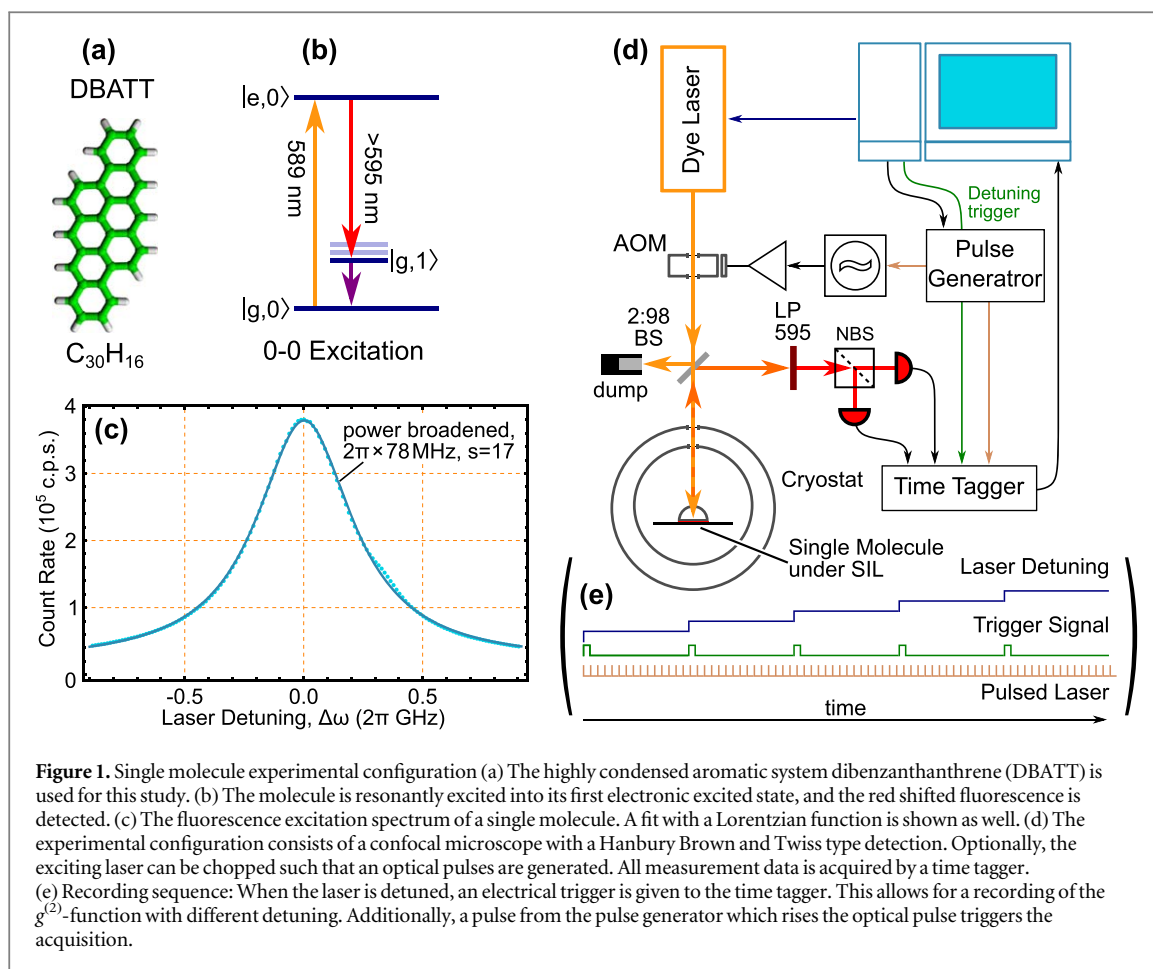
$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho] + \begin{pmatrix} -\Gamma_1 \rho_{22} & -\Gamma_2 \rho_{12} \\ -\Gamma_2 \rho_{12} & \Gamma_1 \rho_{22} \end{pmatrix}. \quad (2)$$

Here, ρ is the density matrix of the assumed two level system and Γ_1 is the spontaneous emission rate and Γ_2 is the total dephasing rate. To fit the experimental outcome of the anti-bunching curve below, the following equation is used [14, 22, 24, 25]. Here τ denotes the detection time after a first successful photon detection event.

$$g^{(2)}(\tau) = 1 - \left(\cos(\Omega_{\text{damp}} \tau) + \frac{\Gamma_1 + \Gamma_2}{2\Omega_{\text{damp}}} \sin(\Omega_{\text{damp}} |\tau|) \right) e^{-1/2(\Gamma_1 + \Gamma_2) |\tau|}. \quad (3)$$

This holds for zero detuning, where Ω_{damp} is the damped Rabi frequency given as $\Omega_{\text{damp}} = \sqrt{\Omega_{\text{Rabi}}^2 - (\Gamma_1 - \Gamma_2)^2/4}$. For an experimental fit an adaption is applied for spurious background contributions, which are considered as incoherent contributions, such as background fluorescence of the matrix, detector noise, etc. This background correction is described in the literature [26].

The recording of the photon statistics with two photon detectors relies on a subsequent detection of two photons. Therefore the coincidence rate is the dominating factor for the recording time of these auto-correlation functions. An interesting alternative is the acquisition of the same signal with an optical pulse. When the laser is off, the molecule is found in the electronic ground state and—if it is off for a longer time—not excited. As the red shifted fluorescence is proportional to the excited state population (ρ_{22}), no photons are expected therefore.



When the light is suddenly switched on, the probability to find the system in the electronic excited state rises initially. Then Rabi oscillation occur and finally the emitter's excited state population approaches a steady-state. This is researched in the following in a pulsed excitation fashion.

3. Experimental

The molecule under study is dibenzanthanthrene (DBATT, $C_{30}H_{16}$, figure 1(a)). It is a highly condensed aromatic system which has been used for cryogenic single molecule studies before [27–30]. Its excitation wavelength is conveniently reached with a rhodamine 6G dye laser, which also covers the excitation into the first vibrational level (see e.g. [28, 29]). A simplified level scheme is shown in figure 1(b). Here, $|g, 0\rangle$ denotes the electronic and vibrational ground state of the molecule, whereas $|e, 0\rangle$ denotes the electronic excited, but vibrational ground state. For these experiments a pure zero-phonon excitation was applied. The laser is spectral narrow-band ($\Delta\nu \approx 2\pi \times 1$ MHz) and delivers up to 1 W continuous wave (CW) emission. Already a few nW focused on a spot of $1 \mu\text{m}$ \varnothing is suitable to saturate the molecule resonantly in a confocal configuration.

The sample is prepared as a diluted solution of DBATT in *n*-tetradecane which is sandwiched between a cover-slide and a solid-immersion lens (SIL, A.W.I. industries, $\varnothing = 3$ mm). In the cryostat and under resonant excitation the molecule emits light on the zero-phonon line and also into the red-shifted levels which correspond to a decay into the manifold of the vibrational excitations of the electronic ground state. The cryogenic conditions are required to freeze out broadening mechanisms from the matrix and to preserve the coherence between the states. Despite the vibrational levels of the electronic ground state, the system can be treated as an almost ideal two-level system, since the decay from the vibrational levels to the ground state occurs in the ps-range. Therefore the flux of the Stokes-shifted photons reports essentially the excited state population of the molecule. The branching ratio between the direct decay into the electronic ground state and to the vibrationally excited levels is estimated to be approx. 50%. At the low power excitation limit, the flux of emitted red-shifted photons is proportional to the incident flux of the excitation laser. When the excitation intensity is increased, the molecular response is non-linear and at a certain point the molecule saturates. The high coherence between the ground and excited states of the molecule and its strong coupling with the external field

implies that the molecule has to be treated by the dressed-state picture [21] and undergoes Rabi-oscillations as discussed below.

Due to stress and strain in the matrix, the resonance frequencies of the zero-phonon line of the molecules is inhomogeneously spread-out on the order of one terahertz. A laser frequency sweep over a couple of hundred megahertz would therefore excite several molecule in the focal volume of a high concentration sample. The linewidth of a single DBATT molecule was reported to be as narrow as $2\pi \times 12.5$ MHz, whereas the average spectral width is on the order of $2\pi \times 15$ – 20 MHz [27, 29]. When the laser is detuned, a fluorescent excitation spectrum is recorded. Such a saturated and power-broadened excitation spectrum of a single molecule is shown in figure 1(c). The linewidth here corresponds to $2\pi \times 78$ MHz and is measured under 380 nW excitation. An estimation in combination with the $g^{(2)}$ -function allows to estimate the natural linewidth of $2\pi \times 16$ MHz. Together with a small amount of dephasing ($T_2^* = 2\pi \times 1.2$ MHz), this fits simultaneous both the spectral recording and the antibunching curve. The saturation parameter is calculated as $\Omega^2 / (T_1 T_2)$ and amounts to 17. Here, the power-broadening increases the linewidth.

Figure 1(d) shows the experimental configuration. A narrow-band dye laser (Coherent 899-29, $\Delta\nu$ ca. $2\pi \times 0.5$ – 1 MHz) is transmitted by a beam splitter (98:2) and excites the molecules. The detected molecular fluorescence is then reflected and detected behind a long-pass filter (Semrock, BrightLine, LP593). Two detectors (Avalanche photo diodes in Geiger mode, APDs, SPCM-AQR, Excellitas) are arranged behind a 50:50 beam-splitter and form a Hanbury Brown and Twiss (HBT) configuration. This is suitable to acquire the photon statistics of the molecule. Cross-talk between the detectors is suppressed by a focal configuration, which implements a $2f/2f$ configuration and does not image one detector to the other. This confocal configuration is sufficient to acquire the anti-bunching of the molecules and the Rabi-oscillations.

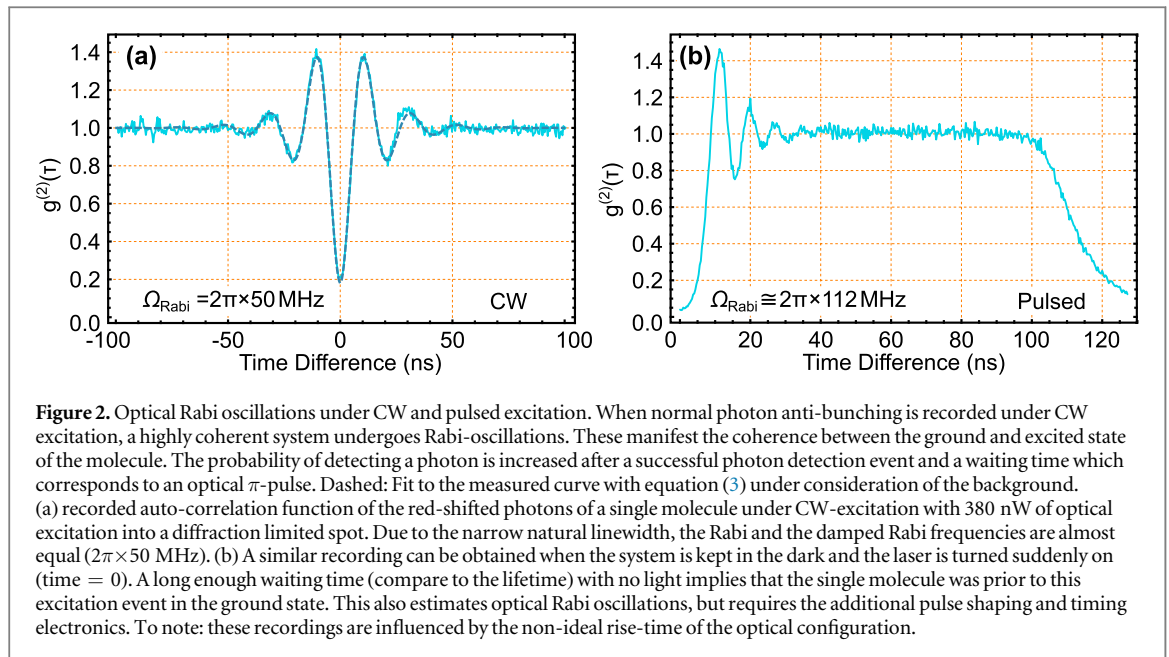
The excitation of a single molecule implies that the emitted photons obey a non-classical photon statistics. No two photons will be emitted at the same time from the single emitter. This is usually tested with the described HBT configuration, and characterizes the waiting time distribution of subsequent photon detection events. The photon arrival times are recorded with the use of a time-tagger, which takes down the photo-detection time with approx. 30 ps accuracy. The exact timing is further influenced by the timing jitter of the APDs of about 500 ps.

For the detuning dependent experiments, an additional channel of the time-tagger was programmed as a trigger input. This is supplied with trigger signals launched with each laser detuning step. It is controlled by a computer measurement card (National Instruments PCI 6229). Each anti-bunching curve is recorded for 50 ms each until the laser is detuned again. When the laser scan is finished, the procedure starts over. By monitoring the detectors individually, the fluorescence excitation spectrum (see e.g. figure 1(c)) is acquired. For the auto-correlation, the detected events are correlated in a ‘start-multiple-stop’ mode, i.e. each event on one detector is correlated with all following events. A simple start-stop measurement would imply a reduced correlation for very large time differences.

Another option to record the detuning dependence of optical Rabi oscillations is to supply the system with an optical pulse. This has been demonstrated already in quantum dots [19], defect centers [12] and molecules [15]. Since the radiative lifetime of the molecule is on the order of a few ns, the pulse should ideally have an optical rise-time of significantly less than this. In the visible part of the optical spectrum, this is not easily achievable with a high repetition rate: Normal Pockels-cells require some high voltages which limits their repetition rate. The commonly available LiNbO₃-fiber modulators undergo radiation damage when light below approx. 600 nm is supplied. An AOM can reach down to rise times on the order of 1–2 ns [15], and allows for repetition rates in the MHz-range.

Under pulsed excitation, the molecule is in its ground state before the optical pulse. When the optical pulse is suddenly switched on, the system gets excited and undergoes as before Rabi oscillations. Then the temporal correlation between the pulse-start time and the emitted photons corresponds to the recording of the $g^{(2)}$ -function. The striking advantage is, that *each* detected photon after a certain trigger pulse leads to a recorded signal. Above, always two photon detection events were required to get a signal for the $g^{(2)}$ -function. This decreases the recording time quadratic to the previous recording. The recording for the pulsed excitation Rabi oscillations is performed in 1000 times of 20 ms each. The total recording time amounts to approx. 22.5 s. The Rabi frequency for this recording amounts to $2\pi \times 112$ MHz. At the end of the pulse, the molecular fluorescence decays with its characteristic lifetime. Due to the finite rise- and fall-time of the AOM in the experiment (which is determined as 10.3 ns), this decay time is affected and represents a convolution of the molecular response and the instrument response function. This also holds for the rise of the laser intensity at the beginning of the laser pulse. This recording is not as easy to theoretically model as the recording of the $g^{(2)}$ -function.

The optical pulse for our experiments was implemented by two cascaded acousto optical modulators (AOMs, Panasonic) which are used in a single pass. Both have a base frequency of $2\pi \times 200$ MHz; the light is focused into their crystal, such that the overall rise-time is optimized to 10.3 ns. This was performed by measuring the pulse with a fast photo diode (New Focus, 1601FC-AC) and monitoring the pulse response in an averaged fashion on a fast oscilloscope. The cascaded configuration was chosen to ensure a sufficient extinction



ratio. The pulse length and the exact timing is implemented by a data timing generator (DTG 5274 with DTGM32 output modules, Tektronix). The supply of the base frequency to the AOMs is implemented with two individual controllable rf-generators (SMIQ-03B, Rhode and Schwarz). The rf-switching is realized by a fast microwave switch (Minicircuit ZASWA-2-50DR+), which is cascaded with a mw-amplifier (Minicircuits, ZHL-1-2W+). The pulse shape is then reconfirmed by a direct measurement of the (attenuated) pulse on the APDs with the time-tagging electronics. In the experiments discussed below, a sequence of 100 ns laser off, alternating with 100 ns laser on is used—the optical pulse is a bit shorter due to electrical influences. The experimental pulse is shown in figure 4(a).

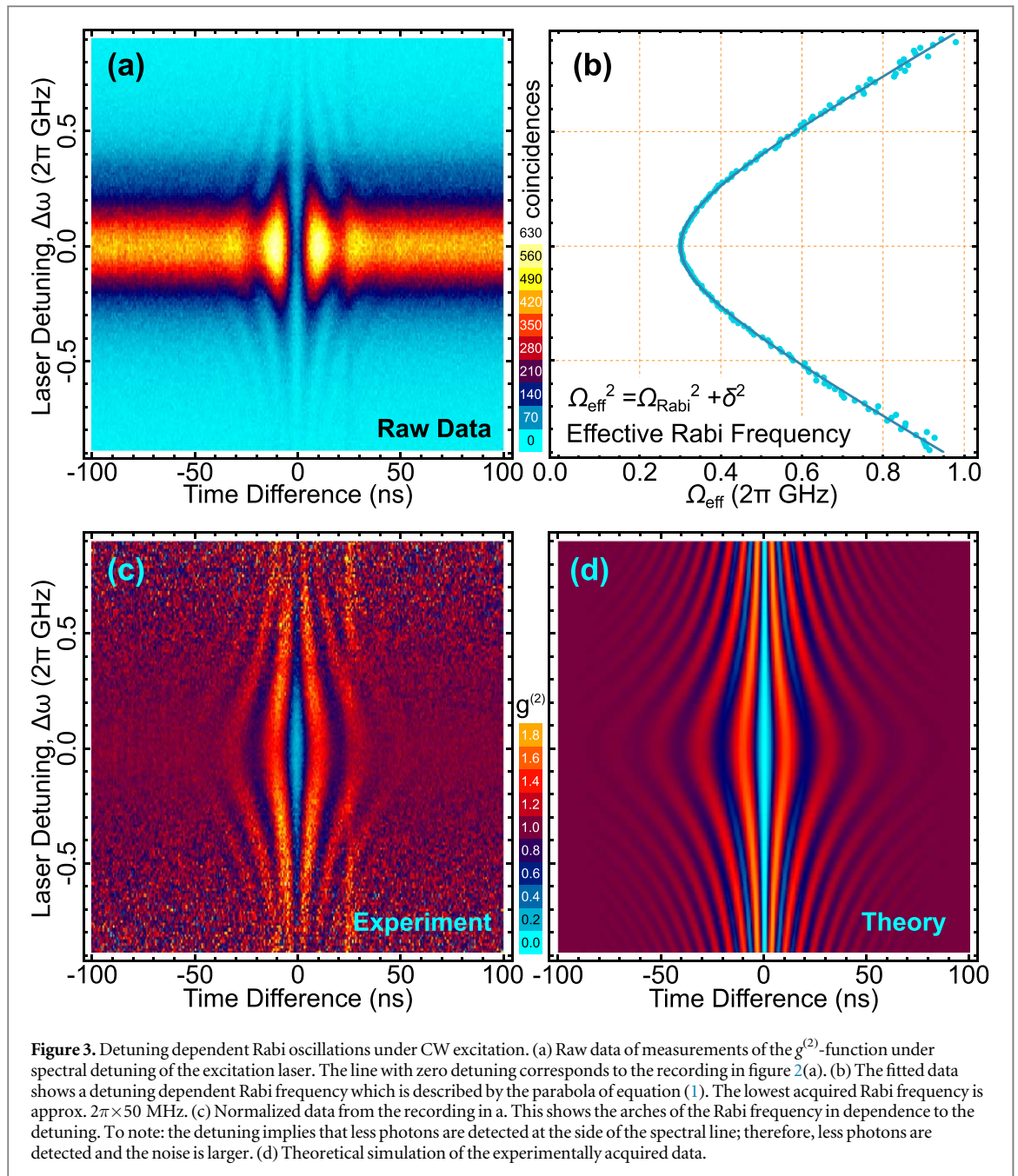
In the pulse regime, instead of a start-stop recording by two APDs, the start is launched from the data timing generator, and the subsequent photon counts are used as stop events. This is performed in 20 ms frequency steps. Here, since only for half of the time the laser is on, the photo-counts which are acquired in one second reduces by a factor of approx. two.

4. Results

Figure 1(c) shows the fluorescence excitation spectrum of a single molecule. The presented spectrum is recorded under saturation with 380 nW excitation power. Therefore the line is power broadened, and a count rate of 380.000 counts per second is observed. As the branching ratio is estimated to be 0.5, an excitation into a higher lying vibrational level of the molecule will lead to approx. the same rate for the spectral narrow-band emission on the zero phonon-line. The small deviations to a perfect Lorentzian line-fit are discussed below.

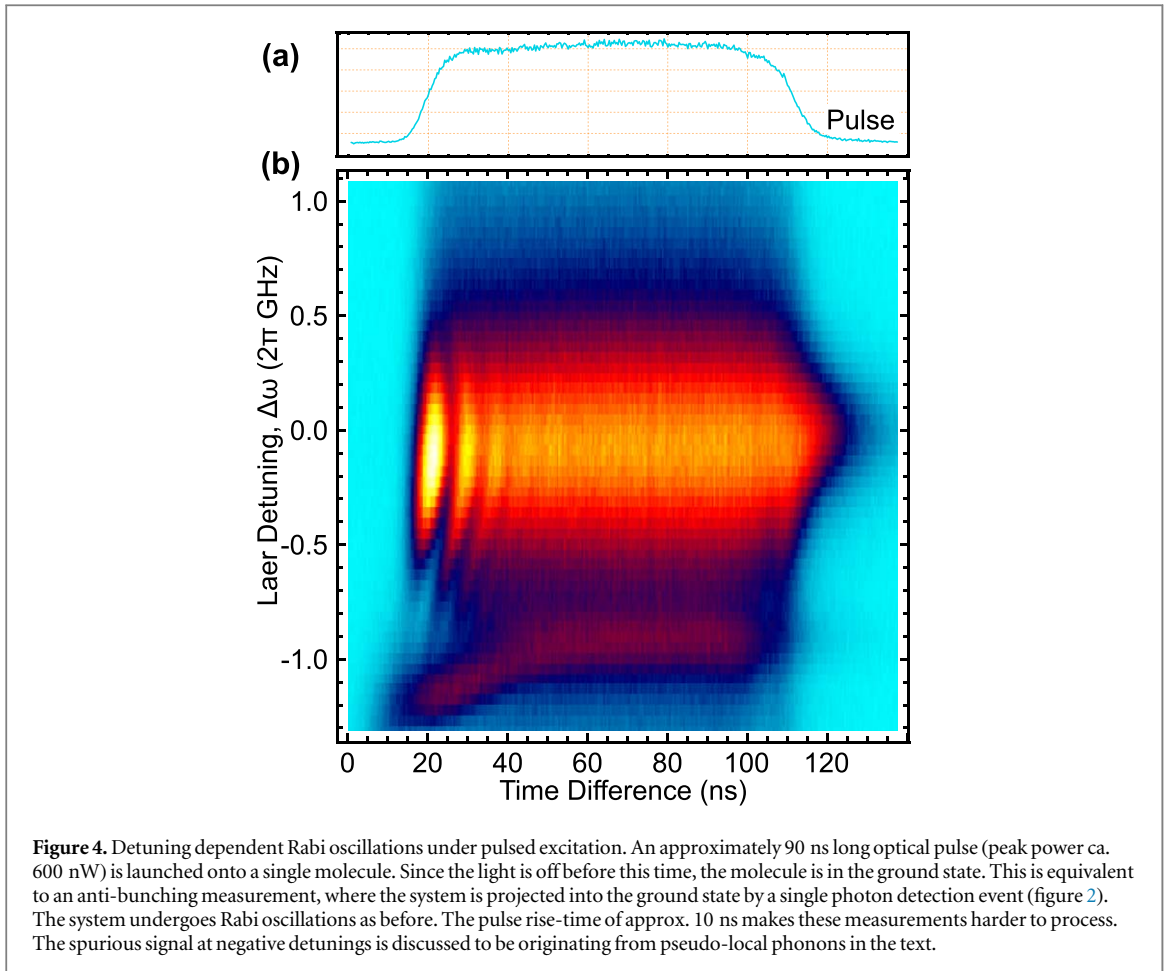
After the recording of the fluorescence excitation scan, the laser is set to the detuning of the highest excitation. Then, the anti-bunching is recorded. This is shown in figure 2(a). It shows the photon anti-bunching in the center of the recording, but also Rabi oscillations. The Rabi frequency is estimated as $2\pi \times 50$ MHz from the oscillations right and left from $\tau = 0$. The curves is well fitted with equation (3) under considering the background. This amounts to approx. 0.18, which is clearly below the limit for multiple emitters of $g^{(2)}(0) = 0.5$. For n independent emitters, the autocorrelation curve amounts to $g^{(2)}(0) = 1 - 1/n$ [22]. The background is accounted to different parameters: the timing jitter of the utilized avalanche photo diodes. The power fluctuations of the laser excitation. The frequency jitter of the laser, as well as spectral diffusion of the molecule. Neighboring molecules and fluorescent background in the sample itself are the most probable cause responsible for this background contribution. For the recording of the anti-bunching, joint detection events are required. Therefore, the coincidence rate and then appropriate measurement time go as the square of the single photon detection rate. The data is acquired in approx. 3700 different recordings with 50 ms recording-time each. The total acquisition time is 185 s for the recording shown in figure 2(a).

As discussed in the experimental section, the experiment is also performed under spectral detuning. This would increase the effective Rabi-frequency as in equation (1), but does also reduce the amount of detected photons per second. This is dramatic, since for the recording of coincidence events the signal scales quadratic with the count rate. So, for a far detuned emitter, longer acquisition times would be necessary to achieve a



comparable signal to noise ratio. Nevertheless, we keep the acquisition time constant, independently of the detuning.

Figure 3(a) shows the raw data of the auto-correlation recording ($G^{(2)}(\tau)$) for a single molecule under spectral detuning. The density plot evaluates 66 528 individual recorded $g^{(2)}$ -functions of 50 ms recording time each. The measurement was performed in 150 frequency steps of $2\pi \times 12.5$ MHz each. Then, this procedure was repeated for 464 times. Two lines where the laser jumped were removed, such that 462 recordings in 150 steps were processed. These laser scans are fitted with a Lorentzian and spectral aligned on their estimated line center. This allows to compensate for laser drifts and eventual instabilities of the single emitter and reduced the 150 frequency steps to 144 frequency steps. Correspondingly, the overall acquisition time was approx. 56 min. The recording corresponds to the unnormalized $G^{(2)}$ -function. The bright horizontal line in the center reflects the high rate of coincidences when the molecule is excited resonantly. The weaker emission on the top and bottom reflect that this is spectral detuned and the molecule emits correspondingly less photons. We like to mention, that a vertical cut through the long time difference section (e.g. right or left of the plot) does *not* reflect the Lorentzian lineshape as it was shown in figure 1(c), since here the recording is based on the joint detection of two photon detection events. Therefore, the width here is narrower as in the case of figure 1(c). When the laser is detuned, the Rabi-frequency increases and reaches up to approx. $2\pi \times 160$ MHz. We like to note that the fitting



in figure 3(b) corresponds to equation (1) with $\Omega_{\text{Rabi}} \approx 2\pi \times 50$ MHz and does not show any unexpected deviations. The curve is fitted according to the raw data acquisition in figure 3(a).

The signal can of course be normalized to one at long times to calculate the usual expected $g^{(2)}$ -function. This normalized signal is shown in the density plot of figure 3(c). Here, the Rabi oscillations at the side of the resonance are more visible. Figure 3(d) shows the theoretical fit to the data. To note that the latter is assumed to be background free; therefore, the probability of receiving a photon at a time difference of zero is assumed to be zero ($g^{(2)}(0) = 0$). The spurious vertical line on the experimental data ($\tau = 23$ ns) results from an electrical cross-talk at the time-tagging unit.

The earlier presented recording of the fluorescence excitation spectrum (figure 1(c)) is acquired under the same conditions and for the same molecule, but only a single detector is evaluated. As in figure 1(c) we also realize a slight asymmetry in this recording (figure 3(a)); a horizontal line on the top shows a small bump which is only present under high power excitation. The origin of this weak contribution is not evident, but it might that another molecule was spectral close, but laterally on another position. Still, one alternative is the presence of pseudo-local phonons, as discussed below.

Figure 4 shows the detuning dependent excitation of the single molecule by an optical pulse as it has been shown earlier in figure 2(b) for the resonant excitation. The incident peak power in this case is 600 nW. The resulting Rabi frequency is $2\pi \times 112$ MHz, which is determined by a fit with equation (3) including a background term, but where the first 8 ns of data were omitted to account for the finite rise-time of the light pulse. The timing advantage for this recording, which represents a different molecule as in figure 3 is such that the overall recording time was set by 61500 recordings with 20 ms each. Here again the raw, uncorrected data is shown. We like to note that this recording is not based on photon coincidence detection. Therefore the linewidth is here corresponding to the actual linewidth as it would be recorded in a fluorescence excitation spectrum (cut from bottom to top). As before, in the recording of the $g^{(2)}$ -function, the Rabi-frequency increases with a larger detuning. Also, some spurious shift to larger times is observed from bottom to top. This is likely caused by a detuning dependent chirp of the optical pulse.

The pulsed measurements show some spurious contribution under negative laser detuning. This is visible directly in the raw data and indicates that the description of the excitation spectrum as a simple Lorentzian line is not sufficient—at least for pulsed experiments. Here it still might be a neighboring molecule. Interestingly, the

spurious feature detunes with the timing of the pulse acquisition. This might also hold for a neighboring molecule which interacts with the primarily monitored molecule or the matrix environment in the laser focus. Since the matrix is affected by the steady-state of the monitored molecule, the neighboring molecule can be detuned under this influence. An alternative explanation is the presence of pseudo-local phonons in the vicinity of the molecule. As for single molecules, such an effect has been discussed by NONN and PLAKHOTNIK [31], and recently extended by others [32]. In this special case, one is able to track the contribution over time (left to right in figure 4(c))—when the system has just released one photon, the energy gap is larger as discussed earlier [31].

5. Conclusion

In conclusion we have investigated the detuning dependence of optical Rabi oscillations from a single molecule under cryogenic conditions. These experiments have been performed in the time domain with time tagged photons. The excitation was performed either with CW laser excitation or by optical pulses. Both show the typical behavior as known from atomic physics. As the physics is well known, the experimental implementation is demanding, since effects such as laser drift or spectral diffusion of the molecule might influence the outcome and wash out the signal.

Experimentally, it is shown that the massive recording of thousands of auto-correlation functions is suitable to record detuning dependent Rabi oscillations. Each of the auto-correlation functions is recorded for a time of only 50 ms, the spectral contribution is processed and the individually recorded auto-correlation functions are summed. This technique allows for fine grained data which combine long-term recordings and sub-ns timing resolutions. The spectral drift in the recording which was acquired over the course of approx. 1 h, amounts to less than $2\pi \times 100$ MHz and is likely caused by the laser drift and not by spectral diffusion of the molecular response.

The generation of an optical pulse with a fast rise-time represents an interesting alternative to the CW recording. Unlike before, each detected photon of the molecule can be processed and has a defined timing relative to the pulse beginning. This gives a quadratic speed-up in the corresponding recording. While this represents an advantage, the rise-time of the utilized acousto-optic modulator (10.3 ns) represents a draw-back. This can be overcome with a faster AOM, as discussed before [15].

In future, the described Rabi oscillations might be usable for single emitter localization [33–35]. Further experiments on triggered single photon emission are underway. These would allow to expedite a variety of quantum optical measurements with single molecules [20].

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