Photon indistinguishability measurements under pulsed and continuous excitation

Ross C. Schofield,1 Chloe Clear,2 Rowan A. Hoggart,1 Kyle D. Major,1 Dara P. S. McCutcheon,2 and Alex S. Clark1,++
1Centre for Cold Matter, Blackett Laboratory, Imperial College London, Prince Consort Road, SW7 2AZ, London, United Kingdom
2Quantum Engineering Technology Labs, H. H. Wills Physics Laboratory and Department of Electrical and Electronic Engineering, University of Bristol, BS8 1FD, United Kingdom
(Dated: July 21, 2021)

The indistinguishability of successively generated photons from a single quantum emitter is most commonly measured using two-photon interference at a beam splitter. Whilst for sources excited in the pulsed regime the measured bunching of photons reflects the full wavepacket indistinguishability of the emitted photons, for continuous wave (cw) excitation the inevitable dependence on detector timing resolution and driving strength obscures the underlying photon interference process. Here we derive a method to extract the photon indistinguishability from cw measurements by considering the relevant correlation functions. The equivalence of both methods is experimentally verified through comparison of cw and pulsed excitation of an archetypal source of photons, a single molecule.

Many photonic quantum technologies rely on the quantum interference of photons, including linear optical quantum information processing [1], cluster state generation [2], boson sampling [3], quantum metrology [4], and Bell-state measurements in quantum communication [5] and teleportation schemes [6]. However, this quantum interference is only possible if the photons used are quantum mechanically indistinguishable, and it is therefore paramount when developing a single photon source that the indistinguishability of emitted photons is quantified. While this can in principle be inferred through separate characterisation of the photons’ polarization, spatial, temporal, and frequency modes, a more rigorous method which directly proves their usefulness is to measure the two-photon interference effect itself.

This two-photon interference effect was first shown by Hong, Ou and Mandel using photons probabilistically generated through spontaneous parametric down-conversion of a pump laser in a nonlinear crystal [7]. Since then routes toward generating photons on-demand have emerged [8], for example those using single quantum emitters such as atoms [9], quantum dots [10–13], crystalline defects [14] and single molecules [15]. For these systems it is common to interfere successively emitted photons from a single source by introducing an appropriate delay and mixing the two signals on a beam splitter. The interference is then manifested as a reduction in coincidence counts at the beam splitter outputs, as measured by the second-order correlation function \(g^{(2)}(\tau)\).

If the emitter is excited regularly with a pulsed laser, then the normalised time-integrated difference between \(g^{(2)}(\tau)\) measurements for photons input with perpendicular and parallel polarization directly gives the full photon wavepacket indistinguishability \(\mathcal{I} = \langle \psi_1 | \psi_2 \rangle\), where \(|\psi_1, 2\rangle\) represent the quantum states, or wavefunctions, of the two interfering photons at the point of measurement. This reflects the underlying modal purity of the photons and gives the probability of two-photon interference, sometimes called the coalescence probability [10, 16]. On the other hand, source excitation with a continuous wave (cw) laser is also commonly used [17–20], and the time-resolved \(g^{(2)}(\tau)\) credited with indicating the extent of the two-photon interference phenomenon. However, such measurements are highly dependent on detector timing resolution: the value of \(g^{(2)}(0)\) tends to zero for perfect detector resolution regardless of the photon spectral purity [21], as the measurement is itself effectively a frequency filter. While methods to extract detector resolution independent metrics from cw measurements have been proposed [22], they do not give the unitless indistinguishability measure as found in the pulsed case.

In this paper we derive correlation functions for both pulsed and cw excitation of a single photon emitter and develop a method to determine the full photon wavepacket indistinguishability under cw excitation, taking into account the dependence of the measurement on driving strength. This is experimentally verified through measurements of a single dibenzoterrylene (DBT) molecule in an anthracene host matrix. Pulsed and cw measurements are performed on the same molecule to independently determine \(\mathcal{I}\), showing the correspondence of the two methods. This equivalence provides a useful analysis tool for developing on-demand photon sources from single quantum emitters.

To begin we consider a beam splitter with successively generated photons from a single quantum emitter at its inputs. The emitter is modelled as a two-level system and described by dipole operator \(\sigma = |g\rangle \langle e|\), with \(|e\rangle\) and \(|g\rangle\) the excited and ground states. Under pulsed excitation the unnormalised second-order correlation function describing photon detection coincidences at the outputs for photons with parallel polarization at the inputs is

\[
\mathcal{G}^{(2)}(\tau) = \int_0^\infty dt \left[ P_e(t) P_e(t + \tau) - \langle g^{(1)}(t + \tau, t) \rangle \right]^2, \tag{1}
\]

where the first order-correlation function is \(g^{(1)}(t_1, t_2) = \langle \sigma^\dagger(t_1) \sigma(t_2) \rangle\), the excited state population at time \(t\) is \(P_e(t) = \langle \sigma_{ee}(t) \rangle\) with \(\sigma_{ee} = \sigma^\dagger \sigma\), and the integration...
over $t$ gives a coincidence probability per pulse [23]. For perpendicular input polarizations photon distinguishability is imposed, and the coincidence probability becomes $G^{(2)}_{\perp}(\tau) = \int_0^{\infty} dt P_\parallel(t) P_\parallel(t + \tau)$. A detailed derivation can be found in the Supplemental Material. The photon in-distinguishability is defined as the normalised difference in coincidence events for parallel and perpendicular input polarisations, integrated over all detection time differences $\tau$ [24]:

$$I = \int d\tau \, G^{(2)}_{\perp}(\tau) - \int d\tau \, G^{(2)}_{\parallel}(\tau) \over \int d\tau \, G^{(2)}_{\parallel}(\tau). \quad (2)$$

For the case of a quantum emitter with spontaneous decay rate $\Gamma_1$ and dephasing rate $\Gamma_2 = \Gamma_1/2 + \gamma$ where $\gamma$ represents excess dephasing, we find $I = \Gamma_1/(2\Gamma_2)$.

Under cw excitation conditions, in the steady state the measured coincidences for parallel inputs is found to be

$$g^{(2)}_{\parallel}(\tau) = \frac{1}{2} \lim_{t \to \infty} \frac{g^{(2)}(t, t + \tau) - [g^{(1)}(t + \tau, t)]^2}{2P_\parallel^2}, \quad (3)$$

which in this case is normalised by the square of the excited steady-state population $P_\parallel = \lim_{t \to \infty} P_\parallel(t)$ and we have defined $g^{(2)}(t_1, t_2) = \langle \sigma^\dagger(t_1)\sigma(t_2)\sigma(t_2)\sigma(t_1) \rangle$ [25].

For the case of parallel inputs where the fields can be treated as uncorrelated we have

$$g^{(2)}_{\perp}(\tau) = \frac{1}{2} \lim_{t \to \infty} \frac{g^{(2)}(t, t + \tau) - [g^{(1)}(t, t + \tau)]^2}{2P_\parallel^2}. \quad (4)$$

It is common to consider a reduction in $g^{(2)}_{\parallel}(\tau)$ at $\tau = 0$ as an indication of the probability of two-photon interference and photon purity. However, since $\sigma(t_2)^2 = 0$, it follows that $g^{(2)}(t, t) = 0$, while $g^{(1)}(t, t) = P_\parallel(t)$, and one can therefore see from Eq. (3) that $g^{(2)}_{\parallel}(0) = 0$ regardless of the photon coherence. In experiments deviations from this value arise due to detector imperfections being unable to precisely resolve $\tau = 0$. As such the value of $g^{(2)}_{\parallel}(0)$ at best reflects a combination of the detector response and photon distinguishability. We could, perhaps, integrate over $\tau$ as in the pulsed case, but as these cw quantities give coincidences per unit time and the system is driven, the time-integrals diverge. To overcome this, we propose to first subtract the excited steady-state population which recovers a convergent integral similar to that in Eq. (2), which after cancellations becomes

$$\tilde{I}(S) = \frac{\int d\tau[1 - g^{(2)}_{\parallel}(\tau)] - \int d\tau[1 - g^{(2)}_{\perp}(\tau)]}{\int d\tau[1 - g^{(2)}_{\perp}(\tau)]}, \quad (5)$$

which in general is a function of the cw driving strength described by the saturation parameter $S$. Our crucial observation is that in the limit of weak driving $\tilde{I}(0) = I$, and we see that cw measurement contains the true photon indistinguishability that we seek.

It is not, of course, possible to measure the correlation function at $S = 0$ as no photons are emitted. We therefore seek an analytical expression for $\tilde{I}(S)$, from which $I$ can be extracted. To do so we consider an incoherently driven effective two-level system, obtained by adiabatic elimination of the fast decaying higher energy state used for off-resonant excitation. This is valid provided decay from the pump level at a rate $\beta$ is fast compared to the other system rates ($\beta \gg \Gamma_1, \Gamma_2$). See Supplemental Material for details.

The result is a second order Born-Markov master equation for the effective two-level system density operator $\rho$:

$$\partial_t \rho(t) = \Gamma_1 (L_\sigma |\rho(t)| + SL_\sigma^\dagger |\rho(t)|) + 2\gamma L_\sigma_\sigma^\dagger |\rho(t)|, \quad (6)$$

where $L_\sigma\sigma^\dagger = X \rho(t)X^\dagger - \frac{1}{2} \{X^\dagger X, \rho(t)\}$ is a Lindblad operator. The incoherent driving is captured by the term involving $S = \Omega^2/(\beta \Gamma_1)$ where $\Omega$ is the Rabi frequency between the ground and higher energy pump level. Using this master equation and the quantum regression theorem [26] we find the correlation functions are

$$g^{(2)}(\tau) = 1 - \frac{\nu}{2} e^{-\gamma(1+S)|\tau|} \left( 1 + \mathcal{M} e^{-2\gamma|\tau|} \right), \quad (7)$$

where we have introduced $\nu$ to account for any imperfection in anti-bunching visibility and $\mathcal{M}$ to account for any modal distinguishability with no temporal dependence, such as incoherent sideband emission or polarization mismatch. For perpendicular polarization $g^{(2)}_{\perp}(\tau)$ is given by Eq. (7) with $\mathcal{M} = 0$. Using these in Eq. (5) we find

$$\tilde{I}(S) = \mathcal{M} \frac{\Gamma_1(1 + S)}{\Gamma(1 + S) + 2\gamma}, \quad (8)$$

which allows for cw measurements of $g^{(2)}_{\parallel}(\tau)$ to be integrated at a known $S$ and extrapolated to $S = 0$ to give $I$. The effective two-level system model from which Eq. (8) is derived holds for $\beta \gg \Gamma_1$, which is well within the validity of our system parameters (see Supplemental Material). At high $S$ stimulated emission from $S_{1,n>0}$ leads to deviations from the behaviour described in Eq. (6) [27].

We now turn to indistinguishability measurements of photons emitted by a single DBT molecule to verify our theory. To isolate a single molecule we used a DBT-doped anthracene nanocrystal grown using a re-precipitation technique [28], see Fig. 1(a). This crystal was deposited onto a gold-coated silicon substrate with a $85\,\text{nm}$ silica spacer layer and protected with a $200\,\text{nm}$ thick layer of PVA. The gold mirror increases the collection efficiency of light from the molecule [29]. The sample was cooled to $4.7\,\text{K}$ in a closed-cycle cryostat (Montana Cryostation) that forms part of a confocal microscope shown in Fig. 1(a). A nanocrystal was selected and illuminated with a cw Ti:Sapphire laser (MSquared, SolTiS), directed using the scanning mirrors. Fig. 1(b) shows the energy level diagram of a DBT molecule and the laser frequencies used for excitation. The laser was tuned in frequency to excite a molecule through the $S_{0,0} \rightarrow S_{1,0}$ zero-phonon line (ZPL) transition, around $784\,\text{nm}$, while the red-shifted fluorescence ($>790\,\text{nm}$), shown in Fig. 1(c),
from the $S_{1,0} \rightarrow S_{0,n>0}$ transitions was collected in a multi-mode fiber and detected with a silicon avalanche photodiode (APD).

A single DBT resonance was found at 784.45 nm, and initial characterisation was performed by repeating scans at increasing excitation powers to determine the maximum count rate and linewidth $\Delta \nu$ of the molecule at each power. This was used to determine the dephasing rate $\Gamma_2$ and saturation behaviour of the molecule using the power-broadening relationship $\Delta \nu = \Gamma_2/(\pi \sqrt{1 + S})$ [30]. From this we find $\Gamma_2 = 2\pi \times 35 \pm 4$ MHz. The cw laser was then tuned to 766.67 nm resonant with a $S_{0,0} \rightarrow S_{1,0}$ transition, shown as a blue arrow in Fig. 1(b). The collection was changed to use a single mode fiber and a narrowband (0.15 nm) tunable reflective notch filter positioned before the APDs. The filter response function and the expected effect on the molecule spectrum is shown in the Supplemental Material. Only the coherent emission from the $S_{1,0} \rightarrow S_{0,0}$ ZPL transition will provide measurable interference; the narrowband filter is used to remove emission from the phonon sideband [29] and $S_{1,0} \rightarrow S_{0,n>0}$ transitions. After filtering we expect a ratio of coherent to total emission of $> 99\%$.

To verify single photon emission a Hanbury Brown and Twiss $g^{(2)}(\tau)$ measurement was performed, shown in Fig. 2(a), by splitting the fluorescence directly on a 50:50 beam splitter before two APDs. Fitting the data using [30]

$$g^{(2)}(\tau) = 1 - V e^{-\Gamma_1 (1+S) |\tau|},$$

we find a visibility of $V = 0.98^{+0.02}_{-0.03}$, which when accounting for detector timing jitter gives $V = 1.00^{+0.09}_{-0.03}$ indicating we are observing a single emitter. Accounting for the measured saturation parameter $S$ (see Supplemental Material) we find a population decay rate of $\Gamma_1 = 2\pi \times 40 \pm 2$ MHz. This is independently verified using a time-correlated single photon counting measurement with a pulsed Ti:Sapphire laser (Coherent, Tsunami) which gives $\Gamma_1 = 2\pi \times 39 \pm 3$ MHz. Comparison of the dephasing and population decay rates gives $\Gamma_1/2\Gamma_2 = 0.57 \pm 0.09$, typical at these temperatures due to the excess thermal dephasing [29, 30].

Turning now to measuring indistinguishability using cw two-photon interference, the fluorescence was sent to the fiber-based interferometer shown in Fig. 1(a). A 50:50 fiber beam splitter and delay fiber was used to temporally overlap photons at a second beam splitter, where two-photon interference occurs. A fiber polarisation controller allowed for measurements of photons with parallel or perpendicular polarization. The results of the parallel and perpendicular interference measurements at $S = 1.3 \pm 0.1$ are shown in Fig. 2(b) and (c). The data falls below 0.5 in the parallel case due to photon interference and coalescence. The side dips arise from anti-bunching at different time delays due to the different combinations of possible optical paths [19]. Fitting these side dips determines the $S$ and $V$ parameters. Equation (7), convolved with the detector response function, is plotted over the data using the determined experimental parameters and $M = 0.98$, showing a good correspondence between the measurement and expected result. The non-convolved function is shown as a dashed line. This is repeated for the orthogonal polarization $g^{(2)}_o(\tau)$ measurement, shown in Fig. 2(c), where $M = 0.04$. For
Figure 2. Continuous wave (cw) and pulsed measurements of photon indistinguishability performed on the same molecule. Measurements are in black, and colored curves show theoretical fits with (solid) and without (dashed) accounting for detector response. (a) A cw intensity correlation $g^{(2)}(\tau)$ with theoretical fits using Eq. (9). (b) A cw $g^{(2)}(\tau)$ measurement with theoretical curves using Eq. (7). (c) A cw $g^{(2)}(\tau)$ measurement with theoretical curves using Eq. (7). (d) Extracted $I$ as a function of saturation parameter ($S$). The prediction from Eq. (8) is shown as the solid line, with the shaded region indicating uncertainties in $\Gamma_1$ and $\Gamma_2$. Data points are from Eq. (8) using integration of the data (black) and fitted functions (orange). The data point at $S = 0$ is from pulsed measurements in parts (e) and (f). (e) A pulsed excitation $G^{(2)}_{\perp}(\tau)$ measurement displaying anti-bunching and two-photon interference, with theory curves using Eq. (7), modified to account for the pulsed behaviour. (f) A pulsed excitation $G^{(2)}_{\parallel}(\tau)$ measurement.

A measurement with perfectly orthogonal polarization $\mathcal{M} = 0$, however polarization drift during measurement resulted in a small two-photon interference contribution. This is characterised in the Supplementary Material.

Figure 2(d) shows the ratio of the integrals described in Eq. (5) for measurements taken at $S = 1.3 \pm 0.1$ and $4.4 \pm 0.2$; both values are well within the validity range for our model. Values of $\tilde{I}$ based on the raw data (black) and the de-convolved functions (orange) are shown, and agree within error. Fitting Eq. (8) with $\mathcal{M}$ as the free variable gives $\mathcal{M} = 0.96 \pm 0.01$ and an indistinguishability of $\mathcal{I} = 0.53 \pm 0.01$ at $S = 0$.

To confirm this result, we now turn to using pulsed excitation. We use a pulsed Ti: Sapphire laser (Spectra-Physics, Tsunami) tuned to 766 nm and filtered to a bandwidth of 5 nm to excite the molecule again on a $S_{0,0} \rightarrow S_{1,n>0}$ transition. The parallel and perpendicular correlation functions are shown in Figs. 2(e) and (f), with each normalised to one. Here the $\sim 12.5$ ns laser repetition period is only a few times longer than the $\sim 4$ ns lifetime of the molecule, and as such photons from subsequent pulses partially overlap. When taking the difference between the $G^{(2)}_{\parallel/\perp}(\tau)$ measurements in Eq. (2) contributions from the overlapping side features cancel, though this is not the case in the denominator. This requires fitting to subtract the contribution of side features from the data to give the true integral of the central feature needed to quantify the indistinguishability according to Eq. (2). In doing so we find $\mathcal{I} = 0.48 \pm 0.02$. This is lower than in the cw measurement due to imperfect temporal overlap arising from a mismatch of the fiber delay and the pulse repetition period in our interferometer. This can be accounted for with a correction factor of $e^{-\Gamma_1 \Delta \tau}$ where $\Delta \tau$ is the time difference between the laser repetition period and the delay time from the fiber [31]. This is $0.91 \pm 0.02$ for our setup, and after this correction we find $\mathcal{I} = 0.53 \pm 0.02$, matching the value found through cw excitation. This is in line with the expected $\mathcal{I}$ value when considering $\mathcal{I} = \Gamma_1/2\Gamma_2 \times \mathcal{M} = 0.54 \pm 0.09$, where the polarisation drift (0.95) and branching ratio (0.99) are contributing to $\mathcal{M}$. The indistinguishability is limited primarily by excess thermal dephasing, which greater cooling can eliminate [18, 29]. Additionally, these measurements highlight the potential of single molecules for quantum technology applications [15] when considering their integration into nanophotonic structures such as waveguides [32, 33], patterned polymers [34, 35] and cavities [36].

In this work we have shown a method to extract the full wavepacket indistinguishability of photons from a cw-excited single quantum emitter using two-photon interference measurements. This was experimentally verified by comparing photon indistinguishability found from cw and pulsed measurements performed on a single DBT molecule at cryogenic temperatures. Previous discussion of cw two-photon interference measurements has been
limited to stating $g^{(2)}_{\parallel/\perp}(0)$ values, a metric that is not independent of the detector timing resolution. We note that our underlying theoretical treatment holds for more complex systems. We already account for the coherent excitation to a third energy level and find a suitable parameter range for disregarding coherent effects, and could be expanded to considering the effects of optical cavities on photon emission [13]. The interference of photons from two separate emitters has also been demonstrated with defects in diamond [37, 38], quantum dots [39, 40] and molecules [41]. Our method could be straightforwardly extended to account for the effects of driving on these systems, and could include further parameters such as different central frequencies and dephasing rates of the two emitters used.

In contrast to the pulsed case, determining indistinguishability from cw excitation requires multiple measurements at known pump powers, or a single measurement at a known $S$. However, it allows extraction of the indistinguishability from the raw data, independent of the ratio of emitter lifetime to laser repetition rate. There is also no requirement for the interferometer delay to be a multiple of the laser repetition period, and cw excitation may also be more convenient due to the higher count rates and the greater spectral selectivity provided. These advantages open the possibility of performing multimode quantum interference experiments such as boson sampling [3] with a single cw-driven emitter and appropriate optical delay lines, thereby simplifying experimental demonstrations.

We thank Jon Dyne and Dave Pitman for their expert mechanical workshop support. This work was supported by EPSRC (EP/P030130/1, EP/P01058X/1, EP/R044031/1, EP/S023607/1, and EP/L015544/1), the Royal Society (UF160475), and the ErnaCofund Initiative QuantERA under the European Union’s Horizon 2020 research and innovation programme, Grant No. 731473 (ORQUID Project).

* alex.clark@imperial.ac.uk

[1] E. Knill, R. Laflamme, and G. J. Milburn, Nature 409, 46 (2001).
[2] B. Bell, A. S. Clark, M. S. Tame, M. Halder, J. Fulconis, W. J. Wadsworth, and J. G. Rarity, New J. Phys. 14, 032012 (2012).
[3] M. Bentivegna, N. Spagnolo, C. Vitelli, F. Flamini, V. Giovannetti, S. Lloyd, and L. Maccone, Nat. Photon. 5, 222 (2011).
[4] V. Giovannetti, S. Lloyd, and L. Maccone, Nat. Photon. 5, 222 (2011).
[5] H. de Riedmatten, I. Marcikic, W. Tittel, H. Zbinden, D. Collins, and N. Gisin, Phys. Rev. Lett. 92, 047904 (2004).
[6] D. Llewellyn, Y. Ding, I. I. Faruque, S. Paesani, D. Bacco, R. Santagati, Y.-J. Qian, Y. Li, Y.-F. Xiao, M. Huber, M. Malik, G. F. Sinclair, X. Zhou, K. Rottwitt, J. L. O’Brien, J. G. Rarity, Q. Gong, L. K. Oxenlowe, J. Wang, and M. G. Thompson, Nat. Phys. 16, 148 (2020).
[7] C. K. Hong, Z. Y. Ou, and L. Mandel, Phys. Rev. Lett. 59, 2044 (1987).
[8] M. D. Eisaman, J. Fan, A. Migdall, and S. V. Polyakov, Review of Scientific Instruments 82, 071101 (2011).
[9] M. Hijlkema, B. Weber, H. P. Specht, S. C. Webster, A. Kuhn, and G. Rempe, Nat. Phys. 3, 253 (2007).
[10] C. Santori, D. Fattal, J. Vuˇckovi´c, G. S. Solomon, and Y. Yamamoto, Nature 419, 594 (2002).
[11] N. Somaschi, V. Giesz, L. De Santis, J. C. Loredo, M. P. Almeida, G. Hornecker, S. L. Portalupi, T. Grange, C. Antón, J. Demory, C. Gómez, I. Sagnes, N. D. Lanzillotti-Kimura, A. Lemaître, A. Auffeves, A. G. White, L. Lancio, and P. Senellart, Nat. Photon. 10, 340 (2016).
[12] H. Wang, Y. M. He, T. H. Chung, H. Hu, Y. Yu, S. Chen, X. Ding, M. C. Chen, J. Qin, X. Yang, R. Z. Liu, Z. C. Duan, J. P. Li, S. Gerhardt, K. Winkler, J. Jurkat, L. J. Wang, N. Gregersen, Y. H. Huo, Q. Dai, S. Yu, S. Höfling, C. Y. Lu, and J. W. Pan, Nat. Photon. 13, 770 (2019).
[13] J. Iles-Smith, D. P. S. McCutcheon, A. Nazir, and J. Mork, Nat. Photon. 11, 521 (2017).
[14] I. Aharonovich, S. Castelletto, D. A. Simpson, C.-H. Su, A. D. Greentree, and S. Prawer, Rep. Prog. Phys. 74, 026501 (2011).
[15] C. Toninelli, I. Gerhardt, A. S. Clark, A. Reserbat-Plantey, S. Gützinger, Z. Ristanovic, M. Colautti, P. Lombardi, K. D. Major, I. Deperasiška, W. H. Nernue, F. H. L. Koppens, B. Kozankiewicz, A. Gourdon, V. Sandoghdar, and M. Orrit, Retrieved from http://arxiv.org/abs/2011.05059 (2020).
[16] N. Tomm, A. Javadi, N. O. Antoniadis, D. Najer, M. C. Löbl, A. R. Korsch, R. Schott, S. R. Valentim, A. D. Wieck, A. Ludwig, and R. J. Warburton, Nature Nanotechnology (2021), 10.1038/s41565-020-00831-x.
[17] R. B. Patel, A. J. Bennett, K. Cooper, P. Atkinson, C. A. Nicoll, D. A. Ritchie, and A. J. Shields, Phys. Rev. Lett. 100, 207405 (2008).
[18] J. B. Trebbia, P. Tamatar, and B. Lounis, Phys. Rev. A 82, 063803 (2010).
[19] M. Rezai, J. Wrachtrup, and I. Gerhardt, Physical Review X 8, 031026 (2018).
[20] P. Lombardi, M. Colautti, R. Duquennoy, G. Murtaza, P. Majumder, and C. Toninelli, Retrieved from http://arxiv.org/abs/2012.13055 (2021).
[21] J. Iles-Smith, D. P. S. McCutcheon, J. Mork, and C. Toninelli, Retrieved from http://arxiv.org/abs/2012.13055 (2021).
[22] R. Proux, M. Maraglou, E. Baudin, C. Voisin, P. Rousseau, and C. Diederichs, Phys. Rev. Lett. 114, 207401 (2015).
[23] A. Kiraz, M. Atatüre, and A. Imamoglu, Phys. Rev. A 69, 032305 (2004).
[24] J. Bylander, I. Robert-Philip, and I. Abram, European Physical Journal D 22, 295 (2003).
[25] S. Unsleber, D. P. S. McCutcheon, M. Dambach, M. Lermer, N. Gregersen, S. Höfling, J. Mork, C. Schneider, and M. Kamp, Phys. Rev. B 91, 075413 (2015).
[26] G. Guarnieri, A. Smirne, and B. Vecchi, Phys. Rev. A 90, 022110 (2014).
[27] R. C. Schofield, K. D. Major, S. Grandi, S. Boissier, E. A. Hinds, and A. S. Clark, J. Phys. Commun. 2, 115027 (2018).
[28] S. Pazzagli, P. Lombardi, D. Martella, M. Colautti,
B. Tiribilli, F. S. Cataliotti, and C. Toninelli, ACS Nano 12, 4295 (2018).
[29] C. Clear, R. C. Schofield, K. D. Major, J. Iles-Smith, A. S. Clark, and D. P. S. McCutcheon, Phys. Rev. Lett. 124, 153602 (2020).
[30] S. Grandi, K. D. Major, C. Polisseni, S. Boissier, A. S. Clark, and E. A. Hinds, Phys. Rev. A 94, 063839 (2016).
[31] C. Schneider, P. Gold, C.-Y. Lu, S. Höfling, J.-W. Pan, and M. Kamp, in *Engineering the Atom-Photon Interaction: Controlling Fundamental Processes with Photons, Atoms and Solids*, edited by A. Predojević and M. W. Mitchell (Springer International Publishing, Cham, 2015) pp. 343–361.
[32] S. Boissier, R. C. Schofield, L. Jin, A. Ovvyan, S. Nur, F. H. L. Koppens, C. Toninelli, W. H. P. Pernice, K. D. Major, E. A. Hinds, and A. S. Clark, Nat. Commun. 12, 706 (2021).
[33] D. Rattenbacher, A. Shkarin, J. Renger, T. Utikal, S. Götzinger, and V. Sandoghdar, New J. Phys. 21, 062002 (2019).
[34] C. Ciancico, K. G. Schädler, S. Pazzagli, M. Columatti, P. Lombardi, J. Osmond, C. Dore, A. Mihi, A. P. Ovvyan, W. H. Pernice, E. Berretti, A. Lavacchi, C. Toninelli, F. H. Koppens, and A. Reserbat-Plantey, ACS Photonics 6, 3120 (2019).
[35] R. C. Schofield, D. P. Bogusz, R. A. Hoggarth, S. Nur, K. D. Major, and A. S. Clark, Opt. Mater. Express 10, 1586 (2020).
[36] D. Wang, H. Kelkar, D. Martin-Cano, D. Rattenbacher, A. Shkarin, T. Utikal, S. Götzinger, and V. Sandoghdar, Nat. Phys. 15, 483 (2019).
[37] A. Sipahigil, K. D. Jahnke, L. J. Rogers, T. Teraji, J. Isoya, A. S. Zibrov, F. Jelezko, and M. D. Lukin, Phys. Rev. Lett. 113, 113602 (2014).
[38] H. Bernien, L. Childress, L. Robledo, M. Markham, D. Twitchen, and R. Hanson, Phys. Rev. Lett. 108, 043604 (2012).
[39] E. B. Flagg, A. Muller, S. V. Polyakov, A. Ling, A. Migdall, and G. S. Solomon, Phys. Rev. Lett. 104, 137401 (2010).
[40] R. B. Patel, A. J. Bennett, I. Farrer, C. A. Nicoll, D. A. Ritchie, and A. J. Shields, Nat. Photon. 4, 632 (2010).
[41] R. Lettow, Y. L. A. Rezus, A. Renn, G. Zumofen, E. Ikonen, S. Götzinger, and V. Sandoghdar, Phys. Rev. Lett. 104, 123605 (2010).
Supplemental Material:
Photon indistinguishability measurements under pulsed and continuous excitation

Ross C. Schofield,1 Chloe Clear,2 Rowan A. Hoggarth,1 Kyle D. Major,1 Dara P. S. McCutcheon,2 and Alex S. Clark1,∗
1Centre for Cold Matter, Blackett Laboratory, Imperial College London, Prince Consort Road, SW7 2AZ, London, United Kingdom
2Quantum Engineering Technology Labs, H. H. Wills Physics Laboratory and Department of Electrical and Electronic Engineering, University of Bristol, BS8 1FD, United Kingdom

In this supplement we first derive the indistinguishability of an emitter measured using two-photon interference with a Hong–Ou–Mandel (HOM) interferometer [1] for non-resonant pulsed excitation. This formalism is then extended for continuous wave (cw) excitation considering a coherently driven three-level system. To find an analytical form for extracting indistinguishability, we simplify the system by the adiabatic elimination of the fast decaying higher energy state used for off-resonant excitation. This formalism is extended for the case of differing driving strengths between perpendicular and parallel polarisation alignment of the interferometer. Moreover, the effect of the phonon sideband is accounted for. In the latter half of the supplement we present experimental details. Measurements performed to characterise the DBT molecule used in the main paper are presented. The effect of filtering on the ratio of coherent to total emission is discussed. The experimental parameters of the interferometer are discussed and an equation that accounts for these is presented. Finally, the indistinguishability measurements performed at higher driving strength are shown.

S1. INTERFERENCE THEORY

We seek to derive the general second-order correlation function for the output fields of a two-photon interference experiment. For this set up we have two (positive) input fields \(E_1^+(t)\) and \(E_2^+(t)\) which pass through a 50:50 beam splitter and are related to the (positive) detected fields \(E_3^-(t)\) and \(E_4^+(t)\) by \(E_3^-(t) = \frac{1}{\sqrt{2}}(E_1^+(t) - E_2^+(t))\) and \(E_4^+(t) = \frac{1}{\sqrt{2}}(E_2^+(t) - E_1^+(t))\) [2]. The unnormalised general cross-correlation function for the output fields with parallel polarisation between interferometer arms is

\[
G^{(2)}_\parallel(\tau,t) = \langle E_3^-(t)E_4^+(t+\tau)E_4^+(t+\tau)E_3^+(t) \rangle, \tag{S1}
\]

where the output field \(E_3\) is detected at \(t\) and the output field \(E_4\) is detected at \(t + \tau\) leading us to define \(\tau\) as the time delay between the two detection measurements. Substituting the input fields into Eq. S1 we find

\[
G^{(2)}_\parallel(\tau,t) = \frac{1}{4} \left( \langle E_1^-(t) + E_2^-(t) \rangle \langle E_2^-(t+\tau) - E_1^-(t+\tau) \rangle \langle E_2^+(t+\tau) - E_1^+(t+\tau) \rangle \langle E_1^+(t) + E_2^+(t) \rangle \right). \tag{S2}
\]

Simplifying Eq. S2 as we assume \(E_1^+\) and \(E_2^+\) originate from the same emitter and are statistically independent; we therefore factorise and drop the numbered subscript. Expanding the correlation function in Eq. S2 gives eight terms which are linear in \(\langle E_1^{(+/-)} \rangle\) and two terms in the form \(\langle E_2^{(+/-)}E_1^{(+/-)} \rangle\) which both go to zero, as expectation values linear in ladder operators are zero [3]. We find

\[
G^{(2)}_\parallel(\tau,t) = \frac{1}{2} \left( 4G^{(2)}_{HBT}(t,\tau) - \left| \langle E_1^-(t+\tau) + E_1^+(t) \rangle \right|^2 + \langle E_1^-(t)E_1^+(t) \rangle \langle E_1^-(t+\tau)E_1^+(t+\tau) \rangle \right), \tag{S3}
\]

where \(G^{(2)}_{HBT}(t,\tau) = \frac{1}{4} \langle E_1^-(t)E_1^-(t+\tau)E_1^+(t+\tau)E_1^+(t) \rangle\) is the Hanbury Brown and Twiss second-order correlation function, relating to the case whereby only one input field is incident on the beam splitter.

∗ alex.clark@imperial.ac.uk
A. Pulsed excitation

For the non-resonant pulsed excitation of a quantum emitter we can model a two-level system initially populated in its excited state, with spontaneous decay rate $\Gamma_1$ and excess pure dephasing $\gamma$. The dynamics can be described with the second-order Born-Markov master equation

$$\partial_t \rho(t) = \Gamma_1 \mathcal{L}_\sigma [\rho(t)] + 2\gamma \mathcal{L}_{\sigma_1^2}[\rho(t)],$$

where $\rho(t)$ is the time dependent density operator, $\sigma = |g\rangle \langle e|$ is the dipole operator with $|e\rangle = (1,0)$ and $|g\rangle = (0,1)$ and $\mathcal{L}_X[\rho(t)] = X \rho(t) X^\dagger - \frac{1}{2} \{ X^\dagger X, \rho(t) \}$ is the Lindblad operator. Setting the input fields as single photons emitted from this quantum emitter, in the far field limit we can set $E^{(+)}(t)$ and $E^{(-)}(t)$ to the dipole operators $\sigma(t)$ and $\sigma^\dagger(t)$, where we have dropped numerical factors for clarity.

To model pulsed excitation of this emitter we change variables to the dipole operators and integrate over $t$ to find the unnormalised ensemble average of coincidence events as

$$G^{(2)}_{\parallel \text{PUL}}(\tau) = \frac{1}{2} \int_0^\infty dt \left( \langle \sigma^\dagger(t) \sigma(t) \rangle \langle \sigma^\dagger(t+\tau) \sigma(t+\tau) \rangle - \frac{1}{2} \left| \langle \sigma^\dagger(t+\tau) + \sigma(t) \rangle \right|^2 \right).$$

where $G^{(2)}_{\parallel \text{PUL}}(t, \tau) = 0$ under pulsed excitation for a single photon emitter as $\sigma^2 = 0$ [3]. To find the normalised second order correlation function, we divide by the uncorrelated peak area $A = \int_0^\infty dt \int d\tau \langle \sigma^\dagger(t) \sigma(t) \rangle \langle \sigma^\dagger(t+\tau) \sigma(t+\tau) \rangle$ to find $g^{(2)}_{\perp \text{PUL}}(\tau) = \frac{1}{A} G^{(2)}_{\perp \text{PUL}}(\tau)$. For the case of perpendicular polarisation between interferometer arms the fields are uncorrelated giving

$$G^{(2)}_{\perp \text{PUL}}(\tau) = \frac{1}{2} \int_0^\infty dt \left( \langle \sigma^\dagger(t) \sigma(t) \rangle \langle \sigma^\dagger(t+\tau) \sigma(t+\tau) \rangle \right).$$

We can readily find the indistinguishability of the emitter from these correlation measurements by integrating over $\tau$ to find [4]

$$I = \frac{\int d\tau \ G^{(2)}_{\parallel}(\tau) - \int d\tau \ G^{(2)}_{\perp}(\tau)}{\int d\tau \ G^{(2)}_{\parallel}(\tau)}.$$  \hspace{1cm} (S7)

Substituting in $G^{(2)}_{\parallel \text{PUL}}(\tau)$ and $G^{(2)}_{\perp \text{PUL}}(\tau)$ into Eq. S7 we find

$$I = \frac{\int dt \int d\tau \left| \langle \sigma^\dagger(t + \tau) + \sigma(t) \rangle \right|^2}{\int dt \int d\tau \left( \langle \sigma^\dagger(t) \sigma(t) \rangle \langle \sigma^\dagger(t + \tau) \sigma(t + \tau) \rangle \right)}.$$ 

(S8)

Using quantum regression theorem we can evaluate the correlation function in the numerator of Eq. S8 to give $\left| \langle \sigma^\dagger(t + \tau) \sigma(t) \rangle \right|^2 = \left| \text{Tr}_S \left( \sigma e^{L_1 t} \rho_S(0) e^{-L_1 t} \right) \right|^2 = e^{-2\Gamma_1 t} e^{-\gamma (t + \frac{\tau}{2})^2}$, where $L$ is the Liouvillian super-operator and the initial population resides in the excited state such that $\rho_S(0) = (1,0,0,0)$ [5]. We evaluate the integrand in the denominator using the same approach, to find $\langle \sigma^\dagger(t) \sigma(t) \rangle \langle \sigma^\dagger(t + \tau) \sigma(t + \tau) \rangle = e^{-\Gamma_1 t} e^{-\gamma (t + \tau)^2}$. Performing the integral over both $t$ and $\tau$ we come to the familiar relation

$$I_{\text{pulsed}} = \frac{\Gamma_1}{2 \Gamma_2},$$

(S9)

where $\Gamma_2 = \frac{\Gamma_1}{2} + \gamma$ is the dephasing rate.

B. Continuous driving

For the case of non-resonant cw driving the experimentally determined second-order correlation functions take on a different form; instead of measuring the ensemble average over coincidence events we require the steady-state function taking $t \rightarrow \infty$ giving

$$G^{(2)}_{\parallel \text{CW}}(\tau) = \lim_{t \rightarrow \infty} \frac{1}{2} \left( 4\gamma G^{(2)}_{\parallel \text{HT}}(t, \tau) - \left| \langle E^{(-)}(t + \tau) + E^{(+)}(t) \rangle \right|^2 + \langle E^{(-)}(t) E^{(+)}(t) \rangle \langle E^{(-)}(t + \tau) E^{(+)}(t + \tau) \rangle \right).$$

(S10)
Substituting in the dipole operator as we assume we are in the far field limit as before and normalising this function with the excited steady state population \( \langle \sigma^1 \sigma \rangle_{ss} = \lim_{t \to \infty} \langle \sigma^1(t)\sigma(t) \rangle \) (noting this is defined as \( P_e \) in the main paper), we find

\[
g^{(2)}_{\text{ICW}}(\tau) = \frac{1}{2 \langle \sigma^1 \sigma \rangle_{ss}^2} \left( \lim_{t \to \infty} \left( \langle \sigma^1(t)\sigma^1(t+\tau)\sigma(t+\tau)\sigma(t) \rangle - \left| \langle \sigma^1(t+\tau)\sigma(t) \rangle \right|^2 \right) + \langle \sigma^1 \sigma \rangle_{ss}^2 \right). \tag{S11}
\]

For the case of perpendicular polarisation alignment where the fields are uncorrelated we have

\[
g^{(2)}_{\perp \text{CW}}(\tau) = \frac{1}{2 \langle \sigma^1 \sigma \rangle_{ss}^2} \left( \lim_{t \to \infty} \langle \sigma^1(t)\sigma^1(t+\tau)\sigma(t+\tau)\sigma(t) \rangle + \langle \sigma^1 \sigma \rangle_{ss}^2 \right). \tag{S12}
\]

It is evident that we cannot use the same methodology to find the indistinguishability as in Eq. S8 as this gives a divergent result when integrating over \( \tau \). However, if we subtract the steady-state population squared (the normalisation factor) we have convergent integrals and can postulate that the indistinguishability can be found from

\[
\tilde{I}(S) = \frac{\int d\tau (1 - g^{(2)}_{\text{ICW}}(\tau)) - \int d\tau (1 - g^{(2)}_{\perp \text{CW}}(\tau))}{\int d\tau (1 - g^{(2)}_{\perp \text{CW}}(\tau))}.
\tag{S13}
\]

Substituting in the \( g^{(2)}_{\text{ICW}}(\tau) \) and \( g^{(2)}_{\perp \text{CW}}(\tau) \) into Eq. S13 we find

\[
\tilde{I}(S) = \frac{\int d\tau \lim_{t \to \infty} \left| \langle \sigma^1(t+\tau)\sigma(t) \rangle \right|^2 / \langle \sigma^1 \sigma \rangle_{ss}^2}{\int d\tau \left( 1 - \lim_{t \to \infty} \langle \sigma^1(t)\sigma^1(t+\tau)\sigma(t+\tau)\sigma(t) \rangle / \langle \sigma^1 \sigma \rangle_{ss}^2 \right)}.
\tag{S14}
\]

1. **Coherent non-resonant driving**

![FIG. S1.](image)

(a) Schematic diagram of non-resonant driving from the ground \(|g\rangle\) to a higher vibrational level \(|v\rangle\), modelled by coherent driving with the Rabi frequency \(\Omega\). The fast non-radiative decay rate from \(|v\rangle \to |e\rangle\) is given by \(\beta\). Spontaneous emission from the excited state \(|e\rangle\) is given by \(\Gamma_1\) and pure dephasing is given by \(\gamma\). (b) Effective two level system by adiabatic elimination of the pump level, giving a driving rate \(S\Gamma_1\) with the saturation parameter \(S\).

To check the validity of this postulated form to find indistinguishability from \(\tilde{I}(S)\) in Eq. S14, a three-level non-resonant driving model shown in Fig. S1(a) is considered. Defining the states \(|v\rangle = (1,0,0), |e\rangle = (0,1,0), |g\rangle = (0,0,1)\) and the operators \(\sigma = |g\rangle \langle e|, \sigma_{uv} = |v\rangle \langle g| \) and \(\sigma_{ee} = |e\rangle \langle e|\). The subsequent Born-Markov second-order master equation for this system is

\[
\partial_t \rho(t) = -i[H_S, \rho] + \Gamma_1 \mathcal{L}_\sigma[\rho(t)] + \beta \mathcal{L}_{\sigma_{uv}}[\rho(t)] + 2\Gamma_1 \mathcal{L}_{\sigma_{ee}}[\rho(t)],
\tag{S15}
\]

with \(H_S = \Omega/2(\sigma_{uv} + \sigma_{uv}^\dagger)\) representing the coherent driving with Rabi frequency \(\Omega\). For a typical DBT molecule the decay rate from the first localised vibrational mode is approximately \(\beta \approx 2500 \times \Gamma_1\) [6]. The excited steady state population for this system is \(\rho_{ee}(\infty) = \langle e|\rho(\infty)|e\rangle = \frac{\Gamma_1^2}{\lambda_1^2 + \Gamma_1^2} \). We can set saturation to \(S = \frac{\Omega^2}{\Gamma_1^2}\), as \(\beta \gg \Gamma_1\) which gives \(\rho_{ee}(\infty) = \frac{S}{1 + S(1 + \frac{\Gamma_1}{\beta})} \approx \frac{S}{1 + S}\).
FIG. S2. (a) and (b) \( g_{↓/∥\text{CW}}^{(2)}(\tau) \) calculations from the three level system and effective two level system models for varying driving strengths (a) \( S = 1 \) and (b) \( S = 500 \). (c) Indistinguishability calculated from the three-level system coherent model (solid yellow line). The analytic form of \( \tilde{I}(S) \) from an effective non-resonantly driven two-level system dashed blue. Red line is full photon wavepacket indistinguishability using the parameters of the experimentally measured molecule giving \( \tilde{I} = 57\% \).

Numerical calculations of \( g_{↓\text{CW}}^{(2)}(\tau) \) and \( g_{↑\text{CW}}^{(2)}(\tau) \) for weak \( S = 0.01 \) and strong \( S = 500 \) driving strengths are shown in Fig. S2(a) and (b). The parameters for these calculations are the same as presented in the main manuscript with, \( \Gamma_1 = 2\pi \times 40 \pm 2 \text{ MHz} \) and the dephasing rate \( \Gamma_2 = 2\pi \times 35 \pm 4 \text{ MHz} \). Numerical simulations of \( \tilde{I}(S) \) calculated from \( g_{↓\text{CW}}^{(2)}(\tau) \) and \( g_{↑\text{CW}}^{(2)}(\tau) \) for varying saturation strengths \( S \) are shown in Fig. S2(c).

**Adiabatic elimination of the pump level**

It is advantageous to have an analytical form for \( \tilde{I}(S) \) as this allows for the extraction of indistinguishability from experiment. To do so we derive an effective two-level system by adiabatically eliminating the higher order energy state, see Fig. S1. Starting with the optical Bloch equations for the three level non-resonantly driven system derived from Eq. S15, we find

\[
\dot{\rho}_{vv}(t) = -\frac{i}{2} \Omega^2 (\rho_{vg}(t) - \rho_{gv}(t)) - \beta \rho_{vv}(t),
\]

(S16)

\[
\dot{\rho}_{ee}(t) = -\Gamma_1 \rho_{ee}(t) + \beta \rho_{ve}(t),
\]

(S17)

\[
\dot{\rho}_{gg}(t) = -\frac{i}{2} \Omega^2 (\rho_{vg}(t) - \rho_{gv}(t)) + \Gamma_1 \rho_{ee}(t),
\]

(S18)

\[
\dot{\rho}_{vg}(t) = \frac{i}{2} \Omega^2 (\rho_{gg}(t) - \rho_{vv}(t)) - \beta \rho_{gv}(t),
\]

(S19)

\[
\dot{\rho}_{ge}(t) = -\frac{i}{2} \Omega^2 \rho_{ee}(t) - \frac{\Gamma_1}{2} \rho_{ge}(t) - \gamma \rho_{ge}(t),
\]

(S20)

\[
\dot{\rho}_{ve}(t) = -\frac{i}{2} \Omega^2 \rho_{ee}(t) - \frac{\Gamma_1}{2} \rho_{ve}(t) - \frac{\beta}{2} \rho_{ve}(t) - \gamma \rho_{ve}(t),
\]

(S21)

where \( \rho_{XY}(t) = \langle X|\rho(t)|Y \rangle [7] \). Solving firstly Eq. S19 with an integrating factor to find

\[
\rho_{vg}(t) = \frac{i}{2} \int_0^t dt' e^{-\frac{i}{2}(t-t')(\rho_{gg}(t') - \rho_{vv}(t'))},
\]

(S22)

which can be solved for the case of \( \beta \gg \Omega \) to give \( \rho_{vg}(t) \approx \frac{i \Omega}{\beta}(\rho_{gg}(t) - \rho_{vv}(t)) \), and by similar methodology \( \rho_{vg}(t) \approx -\frac{i \Omega}{\beta}(\rho_{gg}(t) - \rho_{vv}(t)) \). Using these forms for \( \rho_{vg}(t) \) and \( \rho_{vg}(t) \) and substituting into Eq. S16 we find

\[
\dot{\rho}_{vv}(t) = -\frac{\Omega^2}{\beta} \rho_{ee}(t) + \frac{\Omega^2}{\beta} \rho_{gg}(t).
\]

(S23)
Solving Eq. S23 using an integrating factor again we have
\[ \rho_{vv}(t) = \frac{\Omega^2}{\beta} \int_0^t e^{-\frac{\Omega^2+\beta^2}{\beta}(t-t')} \rho_{gg}(t') dt' \approx \ldots \quad (S31) \]
and the perpendicular measurement as
\[ g^{(2)}_{\perp CW}(\tau) = \left( 1 - \frac{1}{2} e^{-\Gamma_1 |\tau|} \right). \quad (S32) \]

Finally, solving Eq. S21 using the same methodology as above we find
\[ \rho_{ee}(t) = -\frac{i}{\Omega} \int_0^t e^{-\frac{(\Gamma_1 S+2\gamma)(t-t')}{\beta}} \rho_{ge}(t') dt' \approx \ldots \quad (S33) \]
\[ \rho_{gg}(t) \approx \Gamma_1 \rho_{ee}(t) - S \Gamma_1 \rho_{gg}(t), \quad (S34) \]
which holds as long as \( \beta \gg \Omega \). We can further manipulate this equality as \( \Omega = \sqrt{\beta S} \), leading to the constraint \( \beta \gg \Gamma_1 \). The final optical Bloch equation to consider is the \( \rho_{ge}(t) \) contribution. This leads to an interesting pre-factor upon substitution of Eq. S23 into Eq. S20, we find
\[ \dot{\rho}_{ge}(t) = -\frac{\Gamma_1}{2} \rho_{ge}(t) - \frac{\Gamma_1}{2} \rho_{ge}(t) - \gamma \rho_{ge}(t), \quad (S35) \]
which for \( \beta \gg \Gamma_2 \) can be simplified to recover the two-level system optical Bloch equation
\[ \dot{\rho}_{ge}(t) = -\frac{\Gamma_1}{2} \rho_{ge}(t) - \frac{\Gamma_1}{2} \rho_{ge}(t) - \gamma \rho_{ge}(t). \quad (S36) \]

### 2. Indistinguishability from cw measurement

Modelling the effective two level system found from the adiabatic elimination using a second-order Born-Markov master equation, we have
\[ \partial_t \rho(t) = \Gamma_1 \mathcal{L}_\sigma[\rho(t)] + \Gamma_1 S \mathcal{L}_{\sigma^1}[\rho(t)] + 2\gamma \mathcal{L}_{\sigma^1}[\rho(t)]. \quad (S37) \]

The driving in this model is captured by the incoherent dissipator with rate \( \Gamma_1 \). Using quantum regression theorem we can explicitly solve the second-order perpendicular and parallel cw correlation functions in Eq. S11 and S12. We do so by solving their constituent parts, firstly finding the excited steady state population \( \langle \sigma^1 \sigma \rangle_{ss} = \lim_{t \to \infty} \text{Tr}_S[\sigma^1 \sigma e^{\mathcal{L}_\sigma t} \rho_S(0)] \) = \( \frac{S}{1+SS} \), where initially the system is populated is in the ground state. The first order correlation function present in \( g^{(2)}_{\parallel CW}(\tau) \) is evaluated to \( \lim_{t \to \infty} \langle \sigma^1(t+\tau) \sigma(t) \rangle = \lim_{t \to \infty} \text{Tr}_S[\sigma^1 e^{\mathcal{L}_\sigma t} \sigma^{e^{\mathcal{L}_\sigma t} \rho_S(0)}] = \frac{S}{1+SS} e^{-\frac{1}{2}(\Gamma_1 (1+S)+2\gamma) |\tau|} \). Lastly we find, \( \lim_{t \to \infty} \langle \sigma^1(t) \sigma^1(t+\tau) \sigma(t) \sigma(t+\tau) \rangle = \lim_{t \to \infty} \text{Tr}_S[\sigma^1 e^{\mathcal{L}_\sigma t} \sigma^{e^{\mathcal{L}_\sigma t} \rho_S(0)} \sigma^1] \) = \( \frac{S^2}{(1+SS)} (1 - e^{-(1+S) \Gamma_1 |\tau|}) \). Putting these together we can express the parallel polarisation alignment second order correlation function as
\[ g^{(2)}_{\parallel CW}(\tau) = \left( 1 - \frac{1}{2} e^{-(1+S) \Gamma_1 |\tau|} - \frac{1}{2} e^{-\Gamma_1 (1+S)+2\gamma) |\tau|} \right), \quad (S38) \]
and the perpendicular measurement as
\[ g^{(2)}_{\perp CW}(\tau) = \left( 1 - \frac{1}{2} e^{-\Gamma_1 (1+S)+2\gamma) |\tau|} \right). \quad (S39) \]
This theory can be extended following the work of Ref. [8] to account for visibility (which in this formalism is inherently 1) and extra decoherence effects with no temporal dependence, as shown in the main text. Using these resultant correlation functions we find the numerator in Eq. S14 as

\[
\int_0^\infty d\tau \lim_{t\to\infty} \left| \langle \sigma^\dagger(t+\tau)\sigma(t) \rangle \right|^2 / \langle \sigma^\dagger\sigma \rangle_{ss}^2 = \frac{1}{\Gamma_1(1+S) + 2\Gamma_1}. \tag{S33}
\]

Similarly, for the denominator of Eq. S14 we have

\[
\int_0^\infty d\tau 1 - \lim_{t\to\infty} \langle \sigma^\dagger(t)\sigma^\dagger(t+\tau)\sigma(t+\tau)\sigma(t) \rangle / \langle \sigma^\dagger\sigma \rangle_{ss}^2 = \frac{1}{\Gamma_1(1+S)}. \tag{S34}
\]

Substituting these into Eq. S14 we find for a two-level system

\[
\tilde{I}_{2LS}(S) = \frac{\Gamma_1(1+S)}{\Gamma_1(1+S) + 2\gamma}. \tag{S35}
\]

In the limit of \( S \to 0 \) we recover the indistinguishability of the system found from the pulsed case \( \tilde{I}_{2LS}(S \to 0) = \frac{\Gamma_1}{\Gamma_1 + 2\gamma} = I \). Considering the case of differing driving strengths for the parallel (\( S_1 \)) and perpendicular (\( S_2 \)) alignment measurements we find

\[
\tilde{I}_{2LS}(S_1, S_2) = \frac{\Gamma_1(1+S_2)}{\Gamma_1(1+S_1) + 2\gamma} + \frac{S_2 - S_1}{1+S_1}. \tag{S36}
\]

To compare results from the two- and three-level system models see Fig. S2(a) and (b), where the parallel and perpendicular second-order correlation functions are compared for extreme \( S \) values. It can be seen that for \( S = 1 \) the two models converge as expected, as we are within the limit of \( \beta \gg ST_1 \). Setting \( S = 500 \) to capture very strong driving, the coherently driven three-level system cross-correlation functions decrease in width, where \( g_{SS}^{(2)}(\tau) \) decreases more than \( g_{SS}^{(2)}(\tau) \). To see how this deviation affects the calculation of \( \tilde{I}(S) \) for the two models, see Fig. S2(c). It can be seen that for strong driving the effective two-level system model breaks down and our analytical form \( \tilde{I}_{2LS}(S) \) is no longer valid. To investigate for what \( S \) this break down occurs at we plot \( \tilde{I}(S) \) for varying \( I \), see Fig S3. We find for the case of maximum indistinguishability \( I = 1 \) the function \( \tilde{I}(S) \) deviates between the two level and three level system models by 0.5% at \( S = 23.3 \pm 0.1 \), for our system parameters. For decreasing \( I \) (as the pure dephasing increases), this break down value of \( S \) increases, where for \( I = 0.5 \) a deviation of 0.5% occurs at \( S = 40.03 \pm 0.1 \). The observed shift in the breakdown of the two-level system model can be explained by looking at Eq. S28. When the excess pure dephasing becomes non-negligible this acts to suppress the saturation parameter present in this equation.

The origin for this deviation stems from including the pump level in the system. By driving to the pump level coherently we capture the possibility for coherent exchange between the ground and pump level, which acts to suppress \( \tilde{I}(S) \). To see how the states evolve in the two different models see Fig. S4, where this coherent exchange can been seen for \( S = 1000 \). From this analysis we can conclude to extract the indistinguishability from a cw measurement using \( \tilde{I}_{2LS}(S) \) in Eq. S35 one must not pump too hard to ensure coherence effects between the ground and pump level can be neglected.
FIG. S4. Evolution of the states given by $\rho_{XX}(t) = \langle X | \rho(t) | X \rangle$ for both the coherently driven three level system and the effective two level system model for various driving strengths, modified by the saturation parameter $S$. The initial offset for $t < 50$ ps between the two models for the excited state is due to some proportion of the population residing in the vibrational level for the three level system model.

**Contribution from a sideband**

Until now we have neglected any effect from phonon side bands. This methodology to find indistinguishability can be readily extended to capture the influence of a broad sideband with annihilation operator $b_k$ for wavevector $k$, frequency $\omega_k$ and electron phonon coupling constant $g_k$. Considering polaron theory we can find the electric field operator by solving the Heisenberg equations of motion to find $E^{(+)}(t) \propto \sigma(t) B_-(t)$ where $B_{\pm} = \exp[\pm \sum_k g_k (b_k^\dagger - b_k) / \omega_k]$ is the phonon bath displacement operator [6, 9]. Substituting this into the cross correlation functions $g^{(2)}_{\perp/\parallel \text{CW}}(\tau)$ and making the assumption that we can factorise out the photon bath correlation functions due to largely differing time scales results in modification to Eq. S14 by the Debye-Waller factor such that

$$\tilde{I}(S) = \frac{\int d\tau |G(\tau)|^2 \lim_{t \to \infty} \left| \langle \sigma^\dagger(t + \tau) \sigma(t) \rangle \right|^2 / \langle \sigma^\dagger \sigma \rangle_{ss}^2 \int d\tau (1 - \lim_{t \to \infty} \langle \sigma^\dagger(t) \sigma^\dagger(t + \tau) \sigma(t + \tau) \sigma(t) \rangle / \langle \sigma^\dagger \sigma \rangle_{ss}^2),$$

where we have defined the bath phonon correlation function $G(\tau) = \langle B_- (\tau) B_+ \rangle$ [10]. Using this methodology it is straightforward to extend this model to include contributions from local vibrational modes as well.
FIG. S5. (a) Data is from scanning the laser across the $S_{0,0} \rightarrow S_{1,0}$ transition whilst monitoring red-shifted fluorescence at increasing excitation powers. The effect of power broadening with high excitation power is visible. Lines are Lorentzian functions fit to extract the linewidth. (b) Data is linewidth at each power from (a), red line is Eq. S38 giving $\Gamma_2 = 2\pi \times 35 \pm 4$ MHz. (c) Data is the count rate from the molecule whilst exciting with blue-detuned 766.67 nm light, blue line is Eq. S39.

**EXPERIMENTAL**

**Molecule Characterisation**

To extract the dephasing rate $\Gamma_2$ and population decay rate $\Gamma_1$ a number of characterisation experiments were performed. The dephasing rate is extracted from performing resonant linescans at a range of excitation powers whilst monitoring the red-shifted fluorescence, as shown in Fig. S5. These are fitted with Lorentzian curves to extract the linewidth [11]. The power-broadening relationship is described by

$$\Delta \nu = \frac{\Gamma_2}{\pi} \sqrt{1 + S}$$

(S38)

with $S = P/P_{\text{sat}}$, where $P$ is excitation power and $P_{\text{sat}}$ is the power at saturation. This can be used to extract the ‘zero-power’ linewidth, or $2\Gamma_2$ from this data. Figure S5(b) shows a plot of this data, with $P_{\text{sat}} = 27 \pm 3$ nW and $\Gamma_2 = 2\pi \times 35 \pm 4$ MHz.

To extract $\Gamma_1$ from the blue-pumped $g^{(2)}(\tau)$ measurement shown in Fig. 2 of the main paper the saturation parameter of the measurement is required. The power is known from measurement of the excitation power, and $P_{\text{sat}}$ is found from a saturation measurement. For the blue excitation a series of 2D spatial scans were performed at increasing power whilst monitoring the fluorescence, as a function of position. These can be fit with 2D-Gaussian curves to extract the maximum count rate at each power [12]. This data can then be fit with a saturation curve of the form

$$R = R_{\infty} \frac{S}{1 + S}$$

(S39)

where $R$ is the measured count rate and $R_{\infty}$ is the maximum count rate. This is shown in Fig. S5(c). We find $P_{\text{sat}} = 0.33(3)$ mW. This can then be used find $\Gamma_1 = 2\pi \times 40 \pm 2$ MHz, as described in the main paper.

**Filtering**

In order to remove background and molecular emission on the zero-phonon-line sideband and vibrational transitions, a narrow reflection filter is used before the interferometer. This filter can easily be tuned, by changing angle relative to the emission, to a specific ZPL wavelength. Figure S6 shows the measured reflection spectrum of the filter and the effect of the convolution of this with a model DBT spectrum. A spectrum from Ref. [6] is recreated using a Lorentzian ZPL and a Poissonian distribution for the phonon sideband. The integrals of these functions are matched to the respective components of the spectrum. Looking at the post-convolution spectrum we find a proportion of coherent ZPL to total collected emission, termed $\alpha$ of $\alpha = 99.7\%$. For indistinguishability we are interested in the probability of two ZPL photons, giving $\alpha^2 = 99.3\%$ [6].

**Interferometer Description**

The relative reflection/transmission coefficients of two fibre beam splitters that make up the interferometer have an affect on the relative magnitudes of features in the $g^{(2)}_{||/\bot \text{CW}}(\tau)$ measurements. This can be described with the
Pulsed Modelling

For the case of matched laser repetition rate and interferometer delay Eq. S40 can be modified to describe the pulsed measurement with

$$G_{\parallel/\perp,\tau}^{(2)}(\tau) = \sum_i \exp(-\Gamma_1(\tau - id\tau)) - \frac{V}{(l_1^2 l_0^2 + r_0^2 r_1^2)(r_0^2 l_1^2 + r_1^2 l_0^2)} \left( r_1^2 t_1^2 (r_0^4 + t_0^4)e^{(-\Gamma_1(1+S)|\tau|)} + M_{\parallel/\perp,\tau}^{(2)} 2r_0^2 r_1^2 t_0^2 t_1^2 e^{(-\Gamma_1(1+S)(|\tau-d\tau|))} + r_0^4 l_0^2 e^{(-\Gamma_1(1+S)(|\tau-d\tau|))} \right),$$

where $V$ is the anti-bunching visibility, $\Gamma_1$ is the population decay rate, $\gamma$ is the excess dephasing, $d\tau$ is the time delay caused by the delay fibre, and $r_0/t_0$ and $r_1/t_1$ are the reflection and transmission amplitude coefficients for the first and second beam splitters respectively. The mode overlap $M_{\parallel/\perp}$ is to account for non-perfect polarisation control during each measurement. This is similar to that found in Ref. [8], but here combined with the driving relationship developed in this work. There are four terms, two corresponding to the anti-bunching (first term) and indistinguishability (second term) contributions to the central feature, and two corresponding to the anti-bunching features at $\pm d\tau$.

Before taking quantum interference measurements the interferometer was independently characterised. We find $t_0 = \sqrt{0.501(1)}$, $t_0 = \sqrt{0.499(1)}$, $r_1 = \sqrt{0.482(1)}$ and $t_1 = \sqrt{0.518(1)}$. The difference in propagation time through the two arms of the interferometer, caused by the long delay fibre in one arm, was 24.75 ns, found from the time difference between the side dips in the $g_{\parallel/\perp}^{(2)}(\tau)$ measurements. As the interferometer is not actively stabilised there was polarisation drift over the length of a measurement. Monitoring the maximised the output of a PBS on one output of the interferometer we find a 2% to 4% reduction in counts over half an hour, approximately the length of time of a single $g_{\parallel/\perp}^{(2)}(\tau)$ measurement. As $I$ is based on the difference between the parallel and perpendicular measurements the polarisation drift on both contributes. This gives an approximately 5% reduction in $M$, and therefore in $I$.

3. Pulsed Modelling
with $i$ an integer describing the number of pulses each peak is away from the central $\tau = 0$, $i = 0$ feature. This does not hold for large timing mismatch between the pulse repetition period and time delay from the unbalanced interferometer. Each peak will have contributions from coincidences with different path combinations and effectively an interferometer-parameter weighted sum of these will modify Eq. S41. More precisely, there are four path combinations for a coincidence count: no delay, no delay; no delay, delay; delay, no delay; delay, delay. Coincidences taking different paths will be offset by the timing mismatch $\pm \Delta \tau$, however the total coincidences per pulse will be unchanged.

From measuring the time difference between photon detections after sending the pulsed laser through a beam splitter we find the pulsed laser has a repetition period of 12.55 ns corresponding to a repetition rate of 79.7 MHz. Comparing this to the interferometer delay found for cw measurements above we find a mismatch of 0.4 ns compared to twice the laser repetition period. The exponential of the ratio of timing mismatch to the emitter lifetime gives the correction factor used for the pulsed excitation measurements in the main manuscript. For our experimental parameters this offset is smaller than the detector timing uncertainty and as such has no discernible effect after Eq. S41 is convolved with the detector response function. Additionally, as we integrate the data directly the pulse area, or total coincidences per pulse, is the property of interest.

**Indistinguishability Measurements**

Figure S7(a) and (b) are presented in the paper as $g_{\perp/\perp}^{(2)}(\tau)$ measurements taken at $S = 1.3 \pm 0.1$. Parameters for the overlaid function are taken from either interferometer characterisation or global fits of the side features. Figure S7(c) and (d) are the same measurements performed with $S = 4.4 \pm 0.2$. The narrowing effect of faster driving [11] is visible when comparing Fig. S7(a) and (b) with Fig. S7(c) and (d). We note that it is also possible to fit the $g_{\parallel/\perp}^{(2)}(\tau)$ measurement to extract $\Gamma_2$ for cases where $\Gamma_2$ cannot be measured through resonant linescans. For the $S = 1.3 \pm 0.1$ $g_{\parallel/\perp}^{(2)}(\tau)$ measurement, fitting with Eq. S40 for $\gamma$, we find $\Gamma_2 = 2\pi \times 35 \pm 5$ MHz.

[1] C. K. Hong, Z. Y. Ou, and L. Mandel, Phys. Rev. Lett. 59, 2044 (1987).
[2] A. Kiraz, M. Atatüre, and A. Imamoglu, Phys. Rev. A 69, 032305 (2004).
[3] S. Unsleber, D. P. S. McCutcheon, M. Dambach, M. Lermer, N. Gregersen, S. Höfling, J. Mørk, C. Schneider, and M. Kamp, Phys. Rev. B 91, 075413 (2015).
[4] J. Bylander, I. Robert-Philip, and I. Abram, Eur. Phys. J. D 22, 295 (2003).
[5] G. Guarnieri, A. Smirne, and B. Vacchini, Phys. Rev. A 90, 22110 (2014).
[6] C. Clear, R. C. Schofield, K. D. Major, J. Iles-Smith, A. S. Clark, and D. P. S. McCutcheon, Phys. Rev. Lett. 124, 153602 (2020).
[7] G. J. De Valcárcel, E. Roldán, and F. Prati, Revista Mexicana de Fisica E 52, 198 (2006).
[8] M. Rezai, J. Wrachtrup, and I. Gerhardt, Phys. Rev. X 8, 031026 (2018).
[9] J. Iles-Smith, D. P. S. McCutcheon, J. Mørk, and A. Nazir, Phys. Rev. B 95, 201305 (2017).
[10] A. Nazir and D. P. S. McCutcheon, J. Phys.: Condens. Matter 28, 103002 (2016).
[11] S. Grandi, K. D. Major, C. Polisseni, S. Boissier, A. S. Clark, and E. A. Hinds, Phys. Rev. A 94, 063839 (2016).
[12] R. C. Schofield, K. D. Major, S. Grandi, S. Boissier, E. A. Hinds, and A. S. Clark, J. Phys. Commun. 2, 115027 (2018).