Controlling photon statistics by Fano-like interference effects in a cavity with two molecules

Lei-Lei Nian and Jing-Tao Lü*
School of Physics and Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, Wuhan 430074, P. R. China
(Dated: June 15, 2020)

We propose a scheme for controlling photon statistics via the Fano-like interference effects in a system consisting of two molecules and a cavity. Under a incoherent pumping, a strong photon antibunching can be achieved in the setup that manifests the Fano resonance, while the bunching behaviors appear in one- and two-molecule emission cases. For the good-cavity limit, the Fano-like effect can drag the photon in coherent and bunched states to antibunching. For the bad-cavity limit, it is possible to optimize the single-photon emission at the level of antibunching. Our results may provide an effective mean to regulate the photon statistics by the Fano effect beyond the photon blockade effects in quantum optics.

I. INTRODUCTION

The investigation of single-photon sources has recently attracted considerable interest because of its potential applications in quantum computation and quantum communication[1–4]. How to create single photon as well as to exploit its various applications constitutes the principle tasks of quantum optics, quantum chemistry, and condensed matter physics. In quantum optics, the single-photon emission can be obtained with help of the photon blockade, which is caused by the strong optical nonlinearity of the considered systems [5–10]. The mechanism of the photon blockade is similar to the Coulomb blockade. Moreover, the destructive quantum interference between different excitation pathways can be used to generate the single-photon emission[11–15]. This situation only meets the requirement of weak nonlinearity of the system, so it is usually called the unconventional photon blockade. In quantum chemistry and condensed matter physics, the means of generating single photon is completely different from that of the photon blockade in quantum optics [16–19]. Recently, the single-photon emission has been observed experimentally in single molecules and molecular chains decoupled from metal substrate driven by the inelastic tunneling electrons injected from a scanning tunneling microscope (STM) tip[20, 21]. In theory, the single-electron tunneling induced single-photon emission has been predicted base on such experiments[22].

In molecule-mediated STM junctions, the coherent coupling between molecular exciton and plasmon cavity provides an effective way to adjust the emission spectrum. The spectrum with Fano line shape is the result of this coupling, which has been observed experimentally[23–25] and explained well by theory[26, 27]. So far, how this coupling affects photon statistics has not been revealed. In fact, the effect of the Fano or Fano-kile interference on photon statistics have been studied in similar systems driven by coherent pumping. When a two-level quantum dot is positioned nearby a silver nanosphere, the surface plasmons supported by the nanosphere can interplay with the quantum dot by dipole-dipole interaction at wavelengths. The resulting coupling can give arise to the Fano resonance, and the photon antibunching can be found in the Fano peak[28]. A similar phenomenon has been observed recently in a coupled quantum dot and single-mode nanophotonic waveguide system[29]. Considering a system with two cavities and one quantum dot, a strongly photon antibunching can be observed by the interference between the coherent light and the super-Poissonian state driven by photon-induced tunneling[12]. In these systems, the optical nonlinearity induced by the interaction between the coherent pumping and the quantum dot or cavity plays a key role in obtaining single-photon emission. In an electrically driven luminescence system, the nonlinearity and the resulting photon blockade vanishes. Therefore, it is necessary to study the effect of Fano and Fano-like interference effects on photon statistics in incoherently driven systems.

In this paper, we propose a general model consisting of two molecules and a optical cavity to study the effect of Fano-like interference on photon statistics in presence of incoherent and continuous pumping. The photons emitted from one- and two-molecule shows a bunching behavior, while a strong antibunching can be achieved in a system with Fano-like interference effects. In fact, the system with one molecule and a cavity can emit antibunched photons for low quantity factor[30, 31]. However, our results show that the single-photon emission can be further optimized by the Fano-like effect at the level of antibunching. More importantly, photons in coherent and bunched states can be easily adjusted to a strong antibunched state by this effect for high quantity factor.

*jtlu@hust.edu.cn

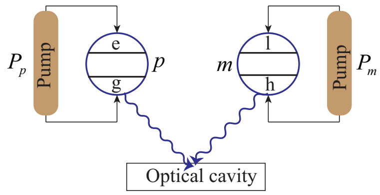

FIG. 1. Schematic representation of the system: two molecules (marked by p and m) and a cavity, the molecules can be excited by the coherent pumping ($\mathcal{P}_p$ and $\mathcal{P}_m$) and they are coupled to a optical cavity by the electron-photon interactions. The dissipations of the molecules and the cavity are not shown here.

II. MODEL

The model is displayed in Fig. 1. The two molecules labeled by p and m can be excited by the incoherent pumping $\mathcal{P}_p$ and $\mathcal{P}_m$, respectively. The excited molecules can further excite the optical cavity. The Hamiltonian of the considered system is

$$\mathcal{H}_s = \mathcal{H}_m + \mathcal{H}_p + \mathcal{H}_{ph} + \mathcal{H}_c, \tag{1}$$

where H_m and H_p describes the uncoupled molecules

$$\begin{aligned} \mathcal{H}_m &= \sum_{i=h,l} \varepsilon_i |i\rangle\langle i|, \\ \mathcal{H}_p &= \sum_{i=g,e} \varepsilon_i |i\rangle\langle i|, \end{aligned} \tag{2}$$

where each molecule contain two well-defined energy levels, that is, h/l (g/e) for p (m) with energies $\varepsilon_{h,l,g,e}$.

The optical cavity is simulated by a single-mode harmonic oscillator with angular frequency ω_p

$$\mathcal{H}_{ph} = (\frac{1}{2} + \hbar\omega_p) a_p^\dagger a_p, \tag{3}$$

The coupling between the two molecules and the cavity in rotating wave approximation is

$$\mathcal{H}_c = m_{ep}(\sigma_m a_p^\dagger + a_p \sigma_m^\dagger) + m_p(\sigma_p a_p^\dagger + a_p \sigma_p^\dagger), \tag{4}$$

where $\sigma_m = |h\rangle\langle l|$ and $\sigma_m^\dagger = |l\rangle\langle h|$ are the annihilation and creation operators of molecular exciton m, respectively. Similarly, the $\sigma_p = |g\rangle\langle e|$ and $\sigma_p^\dagger = |e\rangle\langle g|$ are the excitation and de-excitation of molecular exciton p. m_{ep} and m_p are the exciton-cavity coupling strengths.

III. MASTER EQUATION

Considering the weak interaction between this system and the environment, we can use the master equation to describe the photon transport and statistics. We define the reduced density matrix for the system as ρ by tracing out the environment degrees of freedom in the total density matrix ρ_t, that is, $\rho = \mathrm{Tr}_{en}[\rho_t]$. Under Born-Markovian approximation, the dynamics of ρ satisfies the master equation

$$\begin{aligned} \frac{d}{dt}\rho = &\frac{1}{i\hbar}[\mathcal{H}_s, \rho] + \frac{1}{2}\sum_{\alpha=p,m} \mathcal{P}_\alpha \mathcal{L}[\sigma_\alpha]\rho + \frac{1}{2}\sum_{\alpha=p,m} \gamma_{d\alpha}\mathcal{L}[\sigma_\alpha^\dagger]\rho \\ &+ \frac{\gamma_p}{2} n_B \mathcal{L}[a_p]\rho + \frac{\gamma_p}{2}(1+n_B)\mathcal{L}[a_p^\dagger]\rho, \end{aligned} \tag{5}$$

where $\mathcal{P}_p$ and $\mathcal{P}_m$ are the incoherent and continuous pumping, which can be achieved by external bias voltage. γ_{dp} (γ_{dp}) is the decay rate of the molecular exciton p (m). In the actual current-driven system (e.g. STM junctions), such dissipations may come from the coupling of molecules with electrodes. γ_p is the decay rate of the cavity due to coupled to a photon bath (detector). $n_B = [e^{\hbar\omega_p/k_B T} - 1]^{-1}$ is the average occupation of the cavity mode ω_p in equilibrium state at temperature T. The Lindblad superoperators act according to $\mathcal{L}[\mathcal{A}]\rho = 2\mathcal{A}^\dagger\rho\mathcal{A} - \{\mathcal{A}\mathcal{A}^\dagger, \rho\}$.

To identify the states of the photon in cavity, we can calculate its equal-time k-order coherence function $g^{(k)}(0)$ in the steady state

$$g^{(k)}(0) = \frac{\sum_m \prod_{l=0}^{k-1}(m-l)p_m}{(\sum_m m p_m)^k}, \tag{6}$$

where p_m is the occupation probability of the cavity mode, see Appendix A for details. The photon bunching and antibunching correspond to $g^{(2)}(0) > 1$ and $g^{(2)}(0) < 1$, respectively.

IV. RESULTS

Before showing our results, we need to point out that these two molecules can be placed near a STM tip[21, 32] or a metal nanoparticle[28, 33–35]. Based on this, we take $\mathcal{P}_p = 0.1$ meV, $\mathcal{P}_m = 0.1$ meV, $\gamma_{dp} = 0.05$ meV, $\gamma_{dm} = 0.5$ meV, $m_p = 0.02$ meV, $m_{ep} = 0.2$ meV, $\gamma_p = 0.02$ meV, $\varepsilon_l = 0.5$ eV, $\varepsilon_h = -0.5$ eV, $\varepsilon_e = 0.5$ eV, $\varepsilon_g = -0.5$ eV, and $\hbar\omega_p = 1.0$ eV. The above parameters are used throughout the paper, unless it is needed to indicate other values explicitly.

A. Fano-effect induced photon antibunching

We start by showing the effect of Fano effect on photon statistics. First, we set $m_{ep} = 0$ and $\mathcal{P}_m = 0$ to see the simpler case when only one-molecule p emission. As shown in Fig. 2, the photon bunching can be observed in both resonance and non-resonance regions. Once the second molecule m is involved, $m_{ep} \neq 0$ and $\mathcal{P}_m = 0$, a strong photon antibunching appears in resonance case. Note that the molecule m does not excited by the inherent pumping. Therefore, the antibuching behavior is a

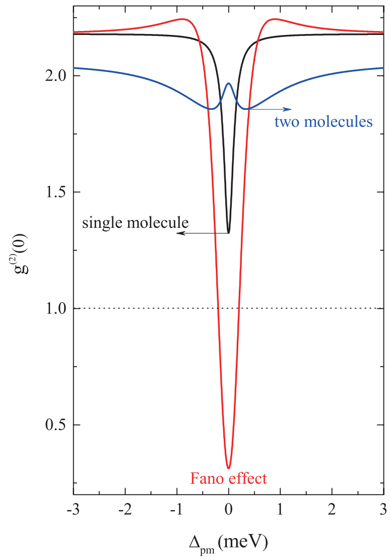

FIG. 2. Second-order photon correlation function $g^{(2)}(0)$ as a function of the energy detuning between molecules and the cavity Δ_{pm}. For single molecule, $\mathcal{P}_p = 0.1$ meV, $\mathcal{P}_m = 0$ meV, $m_p = 0.02$ meV, and $m_{ep} = 0$ meV. For the Fano fluorescence path, $\mathcal{P}_p = 0.1$ meV, $\mathcal{P}_m = 0$ meV, $m_p = 0.02$ meV, and $m_{ep} = 0.2$ meV. For two-molecule emission, $\mathcal{P}_p = 0.1$ meV, $\mathcal{P}_m = 0.1$ meV, $m_p = 0.02$ meV, and $m_{ep} = 0.2$ meV.

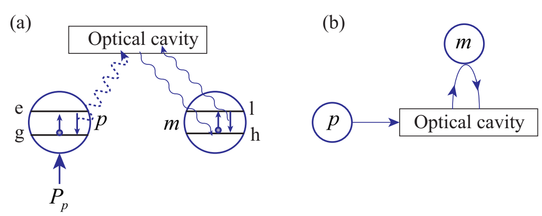

FIG. 3. Schematic of the system of single-molecule emission with Fano-like interference effect. (a) The molecule p can be excited by the pumping $\mathcal{P}_p$, then the excited molecule can further excite the cavity. Without the molecule-cavity coupling, the electron in molecule m is located in the level h. Once the electron-photon interaction turn on, the excited cavity can excite this electron to level l, then the electron can relax to the level l by emitting a photon to the cavity. Thus, the Fano-like path is formed. (b) Simplified diagram of (a), the molecule m can be regarded as a scatter of the cavity excitation.

clear result of Fano-like interference effect. To clarify this effect, we present the corresponding fluorescence path in Fig. 3(a). The electron in molecule p can be excited by the pumping from level g to e, it can again relax to level g by emitting a photon. Thus, the optical cavity can be excited. The excited cavity can further excite the molecule m near it, such that the electron in level h can absorb a photon and then jump to the energy level l. In turn, the relaxation of the electron from l to h excites the cavity. This is illustrated more clearly in Fig. 3(b), one can see that the molecule m can be regarded as a scatter for the excitation of the cavity. This is a evidence of the typical Fano interference effect[36, 37]. When both molecules are excited, the photon is still in bunched state. This further confirms that the photon antibunching is caused by Fano-like interference effect. In fact, for one- and two-molecule emission, a specific Fano interference path cannot be formed. What's more, we can check equal-time *3*-order coherence function $g^{(3)}(0)$ to show that the photon antibunching in our case is not caused by the photon blockade, see Appendix B. These results indicates that the Fano-like effect can be used to achieve strong photon antibunching under incoherent pumping.

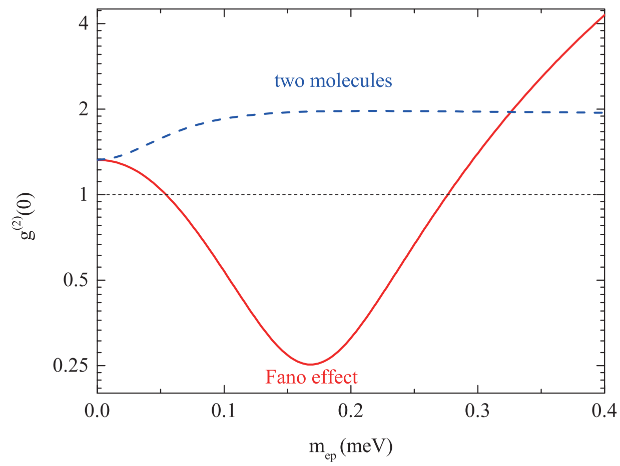

FIG. 4. Semilogarithmic plot of the second-order photon correlation function $g^{(2)}(0)$ as a function of the molecule-cavity coupling strength m_{ep} for the emission with two-molecule and Fano-like interference effect.

Let us further study the effect of Fano effect characterized by the molecule-cavity coupling strength m_{ep} on the photon statistics. Figure 4 shows the $g^{(2)}(0)$ at $\mathcal{P}_m = 0$ and $\mathcal{P}_m = 0.1$ meV as function of the molecule-cavity coupling m_{ep} when the energy detuning vanishes, that is, $\Delta_{mp} = 0$. In experiment, the molecule-cavity coupling strength can be tuned by adjusting the distance between the molecule and the cavity. By increasing m_{ep}, one notices that $g^{(2)}(0)$ initially deceases and then increases after a critical molecule-cavity coupling strength at $m_{ep} \approx 0.18$ meV. Thus, a strong photon antibunching $g^{(2)}(0) \approx 0.25$ can be obtained by the Fano effect. A parallel study for two molecule case that can prove the effect is shown, see the blue dotted line Fig. 4.

B. Effect of quantity factor

We now discuss how the above photon antibunching is affected by the quantity factor Q $(= \hbar\omega_p/\gamma_p)$ of the cavity. For low Q $(m_p, m_{ep} \ll \gamma_p)$ and small pumping $\mathcal{P}_p$, the coupled single molecule and a cavity system shows a near prefect single-photon emission, see the black line in Fig. 5. This is because the cavity lifetime $(\propto 1/\gamma_p)$ is short for low Q, such that the no significant photon population can be stored in the cavity. In this case, the

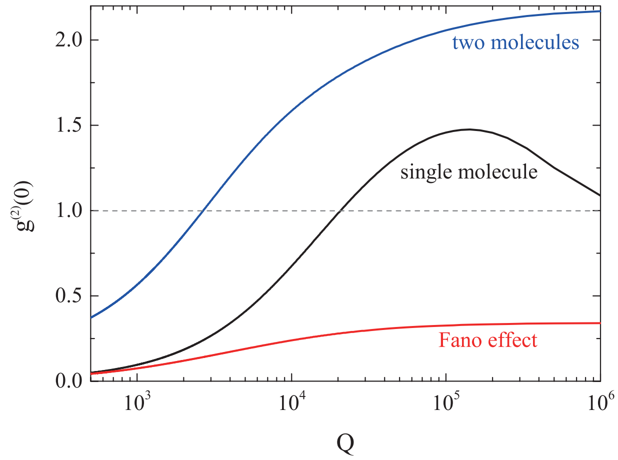

FIG. 5. Second-order photon correlation function $g^{(2)}(0)$ as a function of the quantity factor for three different cases as shown in Fig. 2.

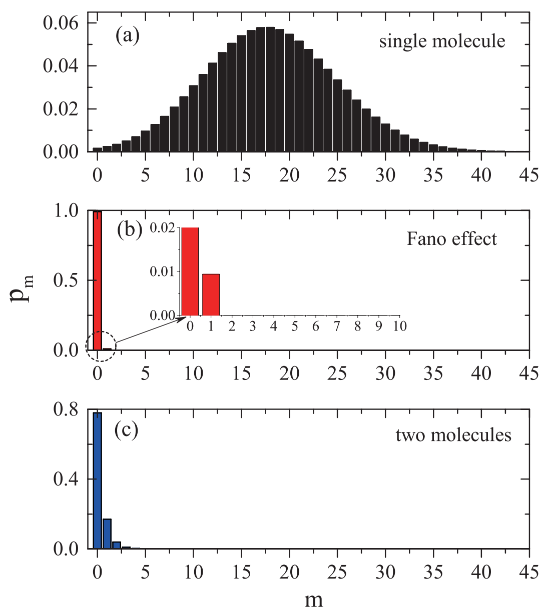

FIG. 6. The occupation probability of the cavity mode p_m corresponding to Fig. 5 at $Q = 10^6$.

emission of the two-level molecule is close to the state without cavity modulation, then $g^{(2)}(0) \approx 0$ can be observed, as studied in previous studies[30, 31]. In the bad cavity limit, we can simulate the photon statistics of single-molecule emission driven by inelastic current injected from a STM tip[20], see Appendix B. Compared with one- and two-molecule emission, the Fano effect can optimize single-photon emission while maintaining a desired level of antibunching, see the blue and red lines in Fig. 5. A recent experiment may be explained by this result[21]. For high Q ($m_p, m_{ep} \gg \gamma_p$), the photon can be stored effectively in the cavity. Thus, the condition of laser lasing as expected is easily achieved in the case of single molecule, then $g^{(2)}(0) \approx 1$ [black line in Fig. 5] and the photon statistics obey Poisson distribution [Fig. 6(a)]. Interestingly, the Fano effect can drag the coherent photon to the antibunched state with a sub-Poisson distribution, see Fig. 6(b). Also, the photon bunching from two-molecue emission can be converted to antibunching with a super-Poisson distribution by the Fano effect, see Fig. 6(c). Our results indicates that the cavity can be bunched, antibunched, or coherent depending on the Fano effect.

V. CONCLUSIONS

In summary, we have studied the the photon statistics of molecules-cavity system that consists of two molecule and a optical cavity. By applying a incoherent pumping to one of the molecules, a photon bunching can be observed. Once the second molecule without pumping is introduced, a strong photon antibunching induced by the Fano-like interference effects appears. The two-molecule emission with equal pumping can further confirm the effect. At the good-cavity limit, the cavity can reach bunched, antibunched, or coherent depending on the Fano effect. At the bad-cavity limit, we can optimize the single-photon emission by this effect at the level of antibunching. Our results may provide a way to control the photon statistics beyond the photon blockade in quantum optics.

ACKNOWLEDGMENTS

This work is financially supported by the National Natural Science Foundation of China (Grant No. 21873033), the National Key Research and Development Program of China (Grant No. 2017YFA0403501) and the program for HUST academic frontier youth team.

Appendix A: Matrix elements of the density operator

We can define the molecule-cavity reduced density operator

$$\rho_{m,n}^{ij,i'j'} := \langle m, i, i'|\rho|j', j, n\rangle, \tag{A1}$$

where $i, j = h, l$ and $i', j' = g, e$. m, n represent the photon Fock states in the cavity. The Coulomb interaction between two levels in each molecule is assumed very strong, such that only one additional electron can occupy the molecule at a time. In this case, for given m and n, 16 linear equations for the matrix elements can be obtained

$$\begin{aligned}\frac{d}{dt}\rho^{hh,gg}_{m,n} &= -i\omega_p(m-n)\rho^{hh,gg}_{m,n} + \gamma_{dm}\rho^{ll,gg}_{m,n} - \mathcal{P}_m\rho^{hh,gg}_{m,n} + \gamma_{dp}\rho^{hh,ee}_{m,n} - \mathcal{P}_p\rho^{hh,gg}_{m,n} \\ &- im_{ep}(\sqrt{m}\rho^{lh,gg}_{m-1,n} - \sqrt{n}\rho^{hl,gg}_{m,n-1}) - im_p(\sqrt{m}\rho^{hh,eg}_{m-1,n} - \sqrt{n}\rho^{hh,ge}_{m,n-1}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n+1}\rho^{hh,gg}_{m+1,n+1} - (m+n)\rho^{hh,gg}_{m,n}].\end{aligned} \tag{A2}$$

$$\begin{aligned}\frac{d}{dt}\rho^{hh,ee}_{m,n} &= -i\omega_p(m-n)\rho^{hh,ee}_{m,n} + \gamma_{dm}\rho^{ll,ee}_{m,n} - \mathcal{P}_m\rho^{hh,ee}_{m,n} - \gamma_{dp}\rho^{hh,ee}_{m,n} + \mathcal{P}_p\rho^{hh,gg}_{m,n} \\ &- im_{ep}(\sqrt{m}\rho^{lh,ee}_{m-1,n} - \sqrt{n}\rho^{hl,ee}_{m,n-1}) - im_p(\sqrt{m+1}\rho^{hh,ge}_{m+1,n} - \sqrt{n+1}\rho^{hh,eg}_{m,n+1}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n+1}\rho^{hh,ee}_{m+1,n+1} - (m+n)\rho^{hh,ee}_{m,n}].\end{aligned} \tag{A3}$$

$$\begin{aligned}\frac{d}{dt}\rho^{hh,ge}_{m,n-1} &= -i\omega_p(m-n+1)\rho^{hh,ge}_{m,n-1} - i(\varepsilon_g - \varepsilon_e)\rho^{hh,ge}_{m,n-1} \\ &+ \gamma_{dm}\rho^{ll,ge}_{m,n-1} - \mathcal{P}_m\rho^{hh,ge}_{m,n-1} - (\frac{\gamma_{dp}}{2} + \frac{\mathcal{P}_p}{2})\rho^{hh,ge}_{m,n-1} \\ &- im_{ep}(\sqrt{m}\rho^{lh,ge}_{m-1,n-1} - \sqrt{n-1}\rho^{hl,ge}_{m,n-2}) - im_p(\sqrt{m}\rho^{hh,ee}_{m-1,n-1} - \sqrt{n}\rho^{hh,gg}_{m,n}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n}\rho^{hh,ge}_{m+1,n} - (m+n-1)\rho^{hh,ge}_{m,n-1}].\end{aligned} \tag{A4}$$

$$\begin{aligned}\frac{d}{dt}\rho^{hh,eg}_{m-1,n} &= -i\omega_p(m-n-1)\rho^{hh,eg}_{m-1,n} - i(\varepsilon_e - \varepsilon_g)\rho^{hh,eg}_{m-1,n} \\ &+ \gamma_{dm}\rho^{ll,eg}_{m-1,n} - \mathcal{P}_m\rho^{hh,eg}_{m-1,n} - (\frac{\gamma_{dp}}{2} + \frac{\mathcal{P}_p}{2})\rho^{hh,eg}_{m-1,n} \\ &- im_{ep}(\sqrt{m-1}\rho^{lh,eg}_{m-2,n} - \sqrt{n}\rho^{hl,eg}_{m-1,n-1}) - im_p(\sqrt{m}\rho^{hh,gg}_{m,n} - \sqrt{n}\rho^{hh,ee}_{m-1,n-1}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m}\sqrt{n+1}\rho^{hh,eg}_{m,n+1} - (m+n-1)\rho^{hh,eg}_{m-1,n}].\end{aligned} \tag{A5}$$

$$\begin{aligned}\frac{d}{dt}\rho^{ll,gg}_{m,n} &= -i\omega_p(m-n)\rho^{ll,gg}_{m,n} - \gamma_{dm}\rho^{ll,gg}_{m,n} + \mathcal{P}_m\rho^{hh,gg}_{m,n} + \gamma_{dp}\rho^{ll,ee}_{m,n} - \mathcal{P}_p\rho^{ll,gg}_{m,n} \\ &- im_{ep}(\sqrt{m+1}\rho^{hl,gg}_{m+1,n} - \sqrt{n+1}\rho^{lh,gg}_{m,n+1}) - im_p(\sqrt{m}\rho^{ll,eg}_{m-1,n} - \sqrt{n}\rho^{ll,ge}_{m,n-1}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n+1}\rho^{ll,gg}_{m+1,n+1} - (m+n)\rho^{ll,gg}_{m,n}].\end{aligned} \tag{A6}$$

$$\begin{aligned}\frac{d}{dt}\rho^{ll,ee}_{m,n} &= -i\omega_p(m-n)\rho^{ll,ee}_{m,n} - \gamma_{dm}\rho^{ll,ee}_{m,n} + \mathcal{P}_m\rho^{hh,ee}_{m,n} - \gamma_{dp}\rho^{ll,ee}_{m,n} + \mathcal{P}_p\rho^{ll,gg}_{m,n} \\ &- im_{ep}(\sqrt{m+1}\rho^{hl,ee}_{m+1,n} - \sqrt{n+1}\rho^{lh,ee}_{m,n+1}) - im_p(\sqrt{m+1}\rho^{ll,ge}_{m+1,n} - \sqrt{n+1}\rho^{ll,eg}_{m,n+1}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n+1}\rho^{ll,ee}_{m+1,n+1} - (m+n)\rho^{ll,ee}_{m,n}].\end{aligned} \tag{A7}$$

$$\begin{aligned}\frac{d}{dt}\rho^{ll,ge}_{m,n-1} &= -i\omega_p(m-n+1)\rho^{ll,ge}_{m,n-1} - i(\varepsilon_g - \varepsilon_e)\rho^{ll,ge}_{m,n-1} \\ &- \gamma_{dm}\rho^{ll,ge}_{m,n-1} + \mathcal{P}_m\rho^{hh,ge}_{m,n-1} - (\frac{\gamma_{dp}}{2} + \frac{\mathcal{P}_p}{2})\rho^{ll,ge}_{m,n-1} \\ &- im_{ep}(\sqrt{m+1}\rho^{hl,ge}_{m+1,n-1} - \sqrt{n}\rho^{lh,ge}_{m,n}) - im_p(\sqrt{m}\rho^{ll,ee}_{m-1,n-1} - \sqrt{n}\rho^{ll,gg}_{m,n}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n}\rho^{ll,ge}_{m+1,n} - (m+n-1)\rho^{ll,ge}_{m,n-1}].\end{aligned} \tag{A8}$$

$$\begin{aligned}\frac{d}{dt}\rho^{ll,eg}_{m-1,n} &= -i\omega_p(m-1-n)\rho^{ll,eg}_{m-1,n} - i(\varepsilon_e - \varepsilon_g)\rho^{ll,eg}_{m-1,n} \\ &- \gamma_{dm}\rho^{ll,eg}_{m-1,n} + \mathcal{P}_m\rho^{hh,eg}_{m-1,n} - (\frac{\gamma_{dp}}{2} + \frac{\mathcal{P}_p}{2})\rho^{ll,eg}_{m-1,n} \\ &- im_{ep}(\sqrt{m}\rho^{hl,eg}_{m,n} - \sqrt{n+1}\rho^{lh,eg}_{m-1,n+1}) - im_p(\sqrt{m}\rho^{ll,gg}_{m,n} - \sqrt{n}\rho^{ll,ee}_{m-1,n-1}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m}\sqrt{n+1}\rho^{ll,eg}_{m,n+1} - (m+n-1)\rho^{ll,eg}_{m-1,n}].\end{aligned} \tag{A9}$$

$$\begin{aligned}\frac{d}{dt}\rho^{hl,gg}_{m,n-1} &= -i\omega_p(m-n+1)\rho^{hl,gg}_{m,n-1} - i(\varepsilon_h-\varepsilon_l)\rho^{hl,gg}_{m,n-1}\\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{hl,gg}_{m,n-1} + \gamma_{dp}\rho^{hl,ee}_{m,n-1} - \mathcal{P}_p\rho^{hl,gg}_{m,n-1}\\ &- im_{ep}(\sqrt{m}\rho^{ll,gg}_{m-1,n-1} - \sqrt{n}\rho^{hh,gg}_{m,n}) - im_p(\sqrt{m}\rho^{hl,eg}_{m-1,n-1} - \sqrt{n-1}\rho^{hl,ge}_{m,n-2})\\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n}\rho^{hl,gg}_{m+1,n} - (m+n-1)\rho^{hl,gg}_{m,n-1}].\end{aligned} \tag{A10}$$

$$\begin{aligned}\frac{d}{dt}\rho^{hl,ee}_{m,n-1} &= -i\omega_p(m-n+1)\rho^{hl,ee}_{m,n-1} - i(\varepsilon_h-\varepsilon_l)\rho^{hl,ee}_{m,n-1}\\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{hl,ee}_{m,n-1} - \gamma_{dp}\rho^{hl,ee}_{m,n-1} + \mathcal{P}_p\rho^{hl,gg}_{m,n-1}\\ &- im_{ep}(\sqrt{m}\rho^{ll,ee}_{m-1,n-1} - \sqrt{n}\rho^{hh,ee}_{m,n}) - im_p(\sqrt{m+1}\rho^{hl,ge}_{m+1,n-1} - \sqrt{n}\rho^{hl,eg}_{m,n})\\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n}\rho^{hl,ee}_{m+1,n} - (m+n-1)\rho^{hl,ee}_{m,n-1}].\end{aligned} \tag{A11}$$

$$\begin{aligned}\frac{d}{dt}\rho^{hl,ge}_{m,n-2} &= -i\omega_p(m-n+2)\rho^{hl,ge}_{m,n-2} - i(\varepsilon_h-\varepsilon_l)\rho^{hl,ge}_{m,n-2} - i(\varepsilon_g-\varepsilon_e)\rho^{hl,ge}_{m,n-2}\\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{hl,ge}_{m,n-2} - (\frac{\gamma_{dp}}{2}+\frac{\mathcal{P}_p}{2})\rho^{hl,ge}_{m,n-2}\\ &- im_{ep}(\sqrt{m}\rho^{ll,ge}_{m-1,n-2} - \sqrt{n-1}\rho^{hh,ge}_{m,n-1}) - im_p(\sqrt{m}\rho^{hl,ee}_{m-1,n-2} - \sqrt{n-1}\rho^{hl,gg}_{m,n-1})\\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n-1}\rho^{hl,ge}_{m+1,n-1} - (m+n-2)\rho^{hl,ge}_{m,n-2}].\end{aligned} \tag{A12}$$

$$\begin{aligned}\frac{d}{dt}\rho^{hl,eg}_{m,n} &= -i\omega_p(m-n)\rho^{hl,eg}_{m,n} - i(\varepsilon_h-\varepsilon_l)\rho^{hl,eg}_{m,n} - i(\varepsilon_e-\varepsilon_g)\rho^{hl,eg}_{m,n}\\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{hl,eg}_{m,n} - (\frac{\gamma_{dp}}{2}+\frac{\mathcal{P}_p}{2})\rho^{hl,eg}_{m,n}\\ &- im_{ep}(\sqrt{m}\rho^{ll,eg}_{m-1,n} - \sqrt{n+1}\rho^{hh,eg}_{m,n+1}) - im_p(\sqrt{m+1}\rho^{hl,gg}_{m+1,n} - \sqrt{n}\rho^{hl,ee}_{m,n-1})\\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n+1}\rho^{hl,eg}_{m+1,n+1} - (m+n)\rho^{hl,eg}_{m,n}].\end{aligned} \tag{A13}$$

$$\begin{aligned}\frac{d}{dt}\rho^{lh,gg}_{m-1,n} &= -i\omega_p(m-1-n)\rho^{lh,gg}_{m-1,n} - i(\varepsilon_l-\varepsilon_h)\rho^{lh,gg}_{m-1,n}\\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{lh,gg}_{m-1,n} + \gamma_{dp}\rho^{lh,ee}_{m-1,n} - \mathcal{P}_p\rho^{lh,gg}_{m-1,n}\\ &- im_{ep}(\sqrt{m}\rho^{hh,gg}_{m,n} - \sqrt{n}\rho^{ll,gg}_{m-1,n-1}) - im_p(\sqrt{m-1}\rho^{lh,eg}_{m-2,n} - \sqrt{n}\rho^{lh,ge}_{m-1,n-1})\\ &+ \frac{\gamma_p}{2}[2\sqrt{m}\sqrt{n+1}\rho^{lh,gg}_{m,n+1} - (m+n-1)\rho^{lh,gg}_{m-1,n}].\end{aligned} \tag{A14}$$

$$\begin{aligned}\frac{d}{dt}\rho^{lh,ee}_{m-1,n} &= -i\omega_p(m-1-n)\rho^{lh,ee}_{m-1,n} - i(\varepsilon_l-\varepsilon_h)\rho^{lh,ee}_{m-1,n}\\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{lh,ee}_{m-1,n} - \gamma_{dp}\rho^{lh,ee}_{m-1,n} + \mathcal{P}_p\rho^{lh,gg}_{m-1,n}\\ &- im_{ep}(\sqrt{m}\rho^{hh,ee}_{m,n} - \sqrt{n}\rho^{ll,ee}_{m-1,n-1}) - im_p(\sqrt{m}\rho^{lh,ge}_{m,n} - \sqrt{n+1}\rho^{lh,eg}_{m-1,n+1})\\ &+ \frac{\gamma_p}{2}[2\sqrt{m}\sqrt{n+1}\rho^{lh,ee}_{m,n+1} - (m+n-1)\rho^{lh,ee}_{m-1,n}].\end{aligned} \tag{A15}$$

$$\begin{aligned}\frac{d}{dt}\rho^{lh,ge}_{m,n} &= -i\omega_p(m-n)\rho^{lh,ge}_{m,n} - i(\varepsilon_l-\varepsilon_h)\rho^{lh,ge}_{m,n} - i(\varepsilon_g-\varepsilon_e)\rho^{lh,ge}_{m,n}\\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{lh,ge}_{m,n} - (\frac{\gamma_{dp}}{2}+\frac{\mathcal{P}_p}{2})\rho^{lh,ge}_{m,n}\\ &- im_{ep}(\sqrt{m+1}\rho^{hh,ge}_{m+1,n} - \sqrt{n}\rho^{ll,ge}_{m,n-1}) - im_p(\sqrt{m}\rho^{lh,ee}_{m-1,n} - \sqrt{n+1}\rho^{lh,gg}_{m,n+1})\\ &+ \frac{\gamma_p}{2}[2\sqrt{m+1}\sqrt{n+1}\rho^{lh,ge}_{m+1,n+1} - (m+n)\rho^{lh,ge}_{m,n}].\end{aligned} \tag{A16}$$

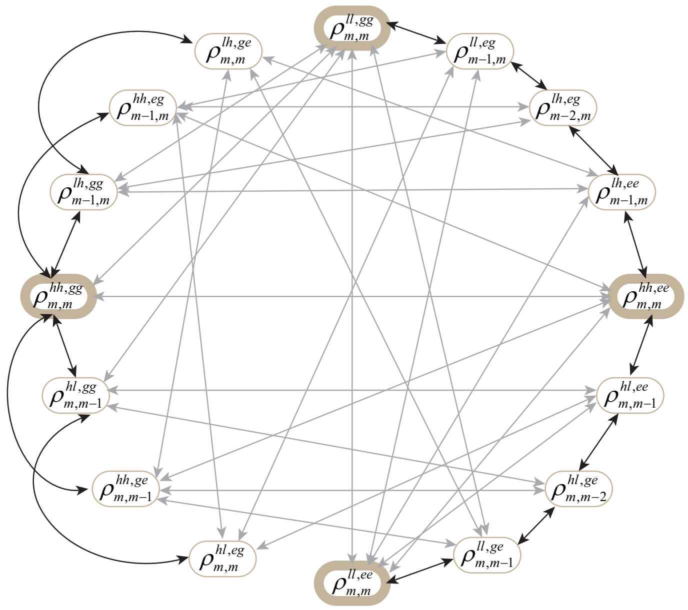

FIG. C1. Self-consistent hierarchy of the dynamical equations.

$$\begin{aligned}\frac{d}{dt}\rho^{lh,eg}_{m-2,n} &= -i\omega_p(m-2-n)\rho^{lh,eg}_{m-2,n} - i(\varepsilon_l-\varepsilon_h)\rho^{lh,eg}_{m-2,n} - i(\varepsilon_e-\varepsilon_g)\rho^{lh,eg}_{m-2,n} \\ &- (\frac{\gamma_{dm}}{2}+\frac{\mathcal{P}_m}{2})\rho^{lh,eg}_{m-2,n} - (\frac{\gamma_{dp}}{2}+\frac{\mathcal{P}_p}{2})\rho^{lh,eg}_{m-2,n} \\ &- im_{ep}(\sqrt{m-1}\rho^{hh,eg}_{m-1,n} - \sqrt{n}\rho^{ll,eg}_{m-2,n-1}) - im_p(\sqrt{m-1}\rho^{lh,gg}_{m-1,n} - \sqrt{n}\rho^{lh,ee}_{m-2,n-1}) \\ &+ \frac{\gamma_p}{2}[2\sqrt{m-1}\sqrt{n+1}\rho^{lh,eg}_{m-1,n+1} - (m+n-2)\rho^{lh,eg}_{m-2,n}].\end{aligned} \tag{A17}$$

Here we consider low temperature limit, $n_B \approx 0$, such that the excitation of the cavity by the photon bath does not exist. In steady state, $\frac{d}{dt}\rho^{ij,i'j'}_{m,n} = 0$, we can get a coupled set of linear equations. Then the occupation probability of the cavity mode p_m can be expressed as

$$p_m = \rho^{hh,gg}_{m,m} + \rho^{hh,ee}_{m,m} + \rho^{ll,gg}_{m,m} + \rho^{ll,ee}_{m,m}. \tag{A18}$$

It is worth pointing out that one must use the normalization condition when solving p_m, that is, $\sum_m(\rho^{hh,gg}_{m,m} + \rho^{hh,ee}_{m,m} + \rho^{ll,gg}_{m,m} + \rho^{ll,ee}_{m,m}) = 1$. The whole coupling scheme of dynamical quantities in right side of Eq. A18 fulfilling a self-consistent hierarchy of dynamical equations as depicted in Fig. C1.

Appendix B: Verification of no photon blockade

According to Eq. 6, we can calculate the equal-time third-order photon correlation function $g^{(3)}(0)$ in Fig. C2. For comparison, the equal-time second-order photon correlation function $g^{(2)}(0)$ discussed in Fig. 2 is also displayed. One can see that $g^{(3)}(0)$ shares the same trand with $g^{(2)}(0)$ but with smaller (stronger) antibunching (bunching) under resonance (non-resonance) mechanism, that is, $g^{(2)}(0) < g^{(3)}(0) < 1$ at $\Delta_{pm} = 0$ and $g^{(3)}(0) > g^{(2)}(0) > 1$ at $\Delta_{pm} \neq 0$, respectively. This violates the definition of the photon blockade[38, 39]. Thus, the photon antibunching in Fig. 2 is not caused by the photon blockade.

Appendix C: Simulations of photon statistics from single-molecule emission in a STM junction

In this section, we simulate the single-photon emission from a single molecule driven by inelastic currents injected from a STM tip[20]. In this experiment, a antibunched photon can be emitted from the decoupled single molecule from the substrate. In our model, we can set $\mathcal{P}_p = 0$ and $m_{ep} = 0$ to simulate the single-photon emission from the

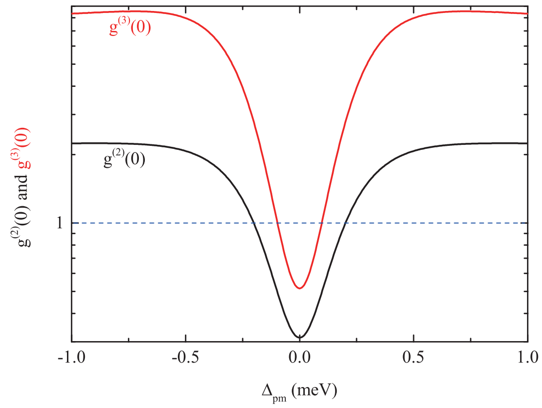

FIG. C2. Second- and third-order photon correlation functions $g^{(2)}(0)$ and $g^{(3)}(0)$ as a function of the energy detuning Δ_{pm}.

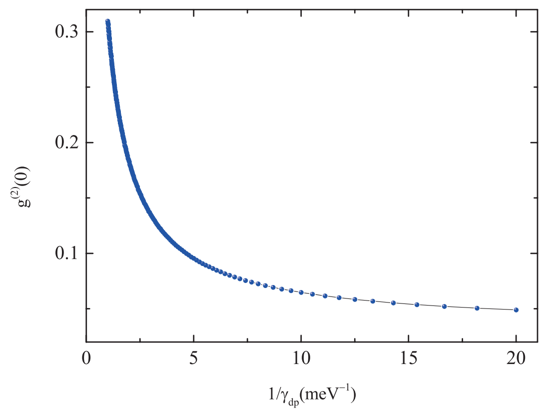

FIG. C3. Second-order photon correlation function $g^{(2)}(0)$ as a function of the inverse of decay rate γ_{dp} of the molecule p.

single molecule as used in this experiment. The main observation of this experiment is that the photon antibunching becomes more and more obvious as the molecule is gradually decoupled from the substrate. We can simulate this process by studying the the evolution of second-order photon correlation function $g^{(2)}(0)$ with the inverse of the decay rate γ_{dp} of the molecule, see Fig. C3. Our results are in good agreement with the experiment, that is, $g^{(2)}(0)$ is decreased by increasing $1/\gamma_{dp}$.

[1] E. Knill, R. Laflamme, and G. J. Milburn, nature **409**, 46 (2001).
[2] P. Walther, K. J. Resch, T. Rudolph, E. Schenck, H. Weinfurter, V. Vedral, M. Aspelmeyer, and A. Zeilinger, Nature **434**, 169 (2005).
[3] T. D. Ladd, F. Jelezko, R. Laflamme, Y. Nakamura, C. Monroe, and J. L. OBrien, Nature **464**, 45 (2010).
[4] V. Scarani, H. Bechmann-Pasquinucci, N. J. Cerf, M. Dušek, N. Lütkenhaus, and M. Peev, Rev. Mod. Phys. **81**, 1301 (2009), `https://link.aps.org/doi/10.1103/RevModPhys.81.1301`.
[5] B. B. Blinov, D. L. Moehring, L.-M. Duan, and C. Monroe, Nature **428**, 153 (2004).
[6] B. Dayan, A. Parkins, T. Aoki, E. Ostby, K. Vahala, and H. Kimble, Science **319**, 1062 (2008).
[7] A. Faraon, I. Fushman, D. Englund, N. Stoltz, P. Petroff, and J. Vučković, Nature Physics **4**, 859 (2008).
[8] P. Rabl, Phys. Rev. Lett. **107**, 063601 (2011), `https://link.aps.org/doi/10.1103/PhysRevLett.107.063601`.
[9] C. Lang, D. Bozyigit, C. Eichler, L. Steffen, J. M. Fink, A. A. Abdumalikov, M. Baur, S. Filipp, M. P. da Silva, A. Blais, and A. Wallraff, Phys. Rev. Lett. **106**, 243601 (2011), `https://link.aps.org/doi/10.1103/PhysRevLett.106.243601`.
[10] C. Hamsen, K. N. Tolazzi, T. Wilk, and G. Rempe, Phys. Rev. Lett. **118**, 133604 (2017), `https://link.aps.org/doi/10.1103/PhysRevLett.118.133604`.
[11] T. C. H. Liew and V. Savona, Phys. Rev. Lett. **104**, 183601 (2010), `https://link.aps.org/doi/10.1103/PhysRevLett.104.183601`.
[12] A. Majumdar, M. Bajcsy, A. Rundquist, and J. Vučković, Phys. Rev. Lett. **108**, 183601 (2012), `https://link.aps.org/doi/10.1103/PhysRevLett.108.183601`.

[13] H. Flayac and V. Savona, Phys. Rev. A **88**, 033836 (2013), https://link.aps.org/doi/10.1103/PhysRevA.88.033836.
[14] X.-W. Xu and Y. Li, Phys. Rev. A **90**, 043822 (2014), https://link.aps.org/doi/10.1103/PhysRevA.90.043822.
[15] J. Li and Y. Wu, Phys. Rev. A **98**, 053801 (2018), https://link.aps.org/doi/10.1103/PhysRevA.98.053801.
[16] Z. Yuan, B. E. Kardynal, R. M. Stevenson, A. J. Shields, C. J. Lobo, K. Cooper, N. S. Beattie, D. A. Ritchie, and M. Pepper, science **295**, 102 (2002).
[17] P. Merino, C. Große, A. Rosławska, K. Kuhnke, and K. Kern, Nature communications **6**, 1 (2015).
[18] A. Rosławska, P. Merino, C. Große, C. C. Leon, O. Gunnarsson, M. Etzkorn, K. Kuhnke, and K. Kern, Nano letters **18**, 4001 (2018).
[19] A. Rosławska, C. C. Leon, A. Grewal, P. Merino, K. Kuhnke, and K. Kern, ACS Nano(2020).
[20] L. Zhang, Y.-J. Yu, L.-G. Chen, Y. Luo, B. Yang, F.-F. Kong, G. Chen, Y. Zhang, Q. Zhang, Y. Luo, *et al.*, Nature communications **8**, 1 (2017).
[21] Y. Luo, G. Chen, Y. Zhang, L. Zhang, Y. Yu, F. Kong, X. Tian, Y. Zhang, C. Shan, Y. Luo, J. Yang, V. Sandoghdar, Z. Dong, and J. G. Hou, Phys. Rev. Lett. **122**, 233901 (2019), https://link.aps.org/doi/10.1103/PhysRevLett.122.233901.
[22] Q. Schaeverbeke, R. Avriller, T. Frederiksen, and F. Pistolesi, Phys. Rev. Lett. **123**, 246601 (2019), https://link.aps.org/doi/10.1103/PhysRevLett.123.246601.
[23] M. C. Chong, G. Reecht, H. Bulou, A. Boeglin, F. Scheurer, F. Mathevet, and G. Schull, Phys. Rev. Lett. **116**, 036802 (2016), https://link.aps.org/doi/10.1103/PhysRevLett.116.036802.
[24] Y. Zhang, Q.-S. Meng, L. Zhang, Y. Luo, Y.-J. Yu, B. Yang, Y. Zhang, R. Esteban, J. Aizpurua, Y. Luo, *et al.*, Nature communications **8**, 1 (2017).
[25] H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura, and Y. Kim, Phys. Rev. Lett. **119**, 013901 (2017), https://link.aps.org/doi/10.1103/PhysRevLett.119.013901.
[26] L.-L. Nian, Y. Wang, and J.-T. Lü, Nano letters **18**, 6826 (2018).
[27] L.-L. Nian and J.-T. Lü, The Journal of Physical Chemistry C **123**, 18508 (2019).
[28] A. Ridolfo, O. Di Stefano, N. Fina, R. Saija, and S. Savasta, Phys. Rev. Lett. **105**, 263601 (2010), https://link.aps.org/doi/10.1103/PhysRevLett.105.263601.
[29] A. P. Foster, D. Hallett, I. V. Iorsh, S. J. Sheldon, M. R. Godsland, B. Royall, E. Clarke, I. A. Shelykh, A. M. Fox, M. S. Skolnick, I. E. Itskevich, and L. R. Wilson, Phys. Rev. Lett. **122**, 173603 (2019), https://link.aps.org/doi/10.1103/PhysRevLett.122.173603.
[30] J. I. Perea, D. Porras, and C. Tejedor, Phys. Rev. B **70**, 115304 (2004), https://link.aps.org/doi/10.1103/PhysRevB.70.115304.
[31] C. Gies, F. Jahnke, and W. W. Chow, Phys. Rev. A **91**, 061804 (2015), https://link.aps.org/doi/10.1103/PhysRevA.91.061804.
[32] Y. Zhang, Y. Luo, Y. Zhang, Y.-J. Yu, Y.-M. Kuang, L. Zhang, Q.-S. Meng, Y. Luo, J.-L. Yang, Z.-C. Dong, *et al.*, Nature **531**, 623 (2016).
[33] A. O. Govorov, J. Lee, and N. A. Kotov, Phys. Rev. B **76**, 125308 (2007), https://link.aps.org/doi/10.1103/PhysRevB.76.125308.
[34] J.-Y. Yan, W. Zhang, S. Duan, X.-G. Zhao, and A. O. Govorov, Phys. Rev. B **77**, 165301 (2008), https://link.aps.org/doi/10.1103/PhysRevB.77.165301.
[35] T. S. Theuerholz, A. Carmele, M. Richter, and A. Knorr, Phys. Rev. B **87**, 245313 (2013), https://link.aps.org/doi/10.1103/PhysRevB.87.245313.
[36] U. Fano, Phys. Rev. **124**, 1866 (1961), https://link.aps.org/doi/10.1103/PhysRev.124.1866.
[37] A. E. Miroshnichenko, S. Flach, and Y. S. Kivshar, Rev. Mod. Phys. **82**, 2257 (2010), https://link.aps.org/doi/10.1103/RevModPhys.82.2257.
[38] A. Miranowicz, M. Paprzycka, Y.-x. Liu, J. c. v. Bajer, and F. Nori, Phys. Rev. A **87**, 023809 (2013), https://link.aps.org/doi/10.1103/PhysRevA.87.023809.
[39] A. Rundquist, M. Bajcsy, A. Majumdar, T. Sarmiento, K. Fischer, K. G. Lagoudakis, S. Buckley, A. Y. Piggott, and J. Vučković, Phys. Rev. A **90**, 023846 (2014), https://link.aps.org/doi/10.1103/PhysRevA.90.023846.