Super- and sub-Poissonian photon statistics for single molecule spectroscopy

Yong He
Department of Chemistry and Biochemistry, Notre Dame University, Notre Dame, Indiana 46556

Eli Barkai
Department of Chemistry and Biochemistry, Notre Dame University, Notre Dame, Indiana 46556
and Department of Physics, Bar Ilan University, Ramat Gan 52900, Israel

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We investigate the distribution of the number of photons emitted by a single molecule undergoing a spectral diffusion process and interacting with a continuous wave laser field. The spectral diffusion is modeled based on a stochastic approach, in the spirit of the Anderson–Kubo line shape theory. Using a generating function formalism we solve the generalized optical Bloch equations and obtain an exact analytical formula for the line shape and Mandel’s $Q$ parameter. The line shape exhibits well-known behaviors, including motional narrowing when the stochastic modulation is fast and power broadening. The Mandel parameter, describing the line shape fluctuations, exhibits a transition from a quantum sub-Poissonian behavior in the fast modulation limit to a classical super-Poissonian behavior found in the slow modulation limit. Our result is applicable for weak and strong laser fields, namely, for arbitrary Rabi frequency. We show how to choose the Rabi frequency in such a way so that the quantum sub-Poissonian nature of the emission process becomes strongest. A lower bound on $Q$ is found and simple limiting behaviors are investigated. A nontrivial behavior is obtained in the intermediate modulation limit, when the time scales for spectral diffusion and the lifetime of the excited state become similar. A comparison is made between our results and previous ones derived, based on the semiclassical generalized Wiener–Khintchine formula. © 2005 American Institute of Physics. [DOI: 10.1063/1.1888388]

I. INTRODUCTION

Physical, chemical, and biological systems are investigated in many laboratories using single molecule spectroscopy. The investigation of the distribution of the number of photons emitted from a single molecule source is the topic of extensive theoretical research, e.g., see Refs. 2–15. Since optical properties of single molecules are usually very sensitive to dynamics and statics of their environment, and since the technique removes the many particle averaging found in conventional measurement techniques, single molecule spectroscopy reveals interesting fluctuation phenomena. An important mechanism responsible for the fluctuations in the number of photons emitted from a single molecule source is spectral diffusion, e.g., see Refs. 16–20. In many cases the absorption frequency of the molecule will randomly change due to different types of interactions between the molecule and its environment (e.g., see Refs. 15 and 21–26, and references therein). For example, for single molecules embedded in low temperature glasses, flipping two level systems embedded in the glassy environment induce stochastic spectral jumps in the absorption frequency of the single molecule under investigation. In this way the molecule may come in and out of resonance with the continuous wave laser field with which it is interacting.

Obviously a second mechanism responsible for fluctuations of photon counts is the quantum behavior of the spontaneous emission process. In his fundamental work Mandel showed that a single atom in the process of resonance fluorescence, in the absence of spectral diffusion, exhibits sub-Poissonian photon statistics. Photon statistics is characterized by Mandel’s $Q$ parameter,

$$Q = \frac{N^2 - \langle N^2 \rangle}{\langle N \rangle} - 1,$$

where $N$ is the number of emitted photons within a certain time interval. The case $Q < 0$ is called sub-Poissonian behavior, while $Q > 0$ is called super-Poissonian. Sub-Poissonian statistics has no classical analog. Briefly, the effect is related to antibunching of photons emitted from a single source and to Rabi oscillations of the excited state population which favors an emission process with some periodicity in time (see details below). Sub-Poissonian photon statistics and photon antibunching were measured in several single molecule and single quantum dots experiments.

In the context of single molecule spectroscopy, the relation between photon counting statistics and spectral diffusion was investigated based on a semiclassical approximation in Refs. 26 and 40. The work in Refs. 26 and 40 yields $Q$ in terms of a Fourier transform of a three time dipole correlation, and hence generalized the Wiener–Khintchine theorem,
which yields the line shape in terms of a one time dipole correlation function. The theorem is based on the semiclassical theory of interaction of light with matter and on linear response theory (i.e., weak Rabi frequency), it yields \( Q > 0 \). As pointed out in Refs. 15, 26, and 41 such a behavior is expected to be valid only for slow enough spectral diffusion processes. An important step beyond the semiclassical approximation was considered by Zheng and Brown. For in particular, they showed, using numerical simulations, that when bath fluctuations are fast enough \( Q < 0 \) even in the limit of long measurement times (see further details below). Hence a fully quantum treatment of photon statistics must be considered. A theoretical treatment of sub-Poissonian statistics is still missing in the quantum limit of fast modulation.

In this paper we obtain an exact analytical expression for the \( Q \) parameter in the long time limit for a single molecule undergoing a stochastic spectral diffusion process. To obtain the exact solution we use the Zheng–Brown generating function method for single molecule photon statistics. For the spectral diffusion we use a simple stochastic approach, in the spirit of the Kubo–Andersen line shape theory. The model exhibits generic behaviors of line shapes of molecules embedded in a condensed phase environment, e.g., motional narrowing when the stochastic fluctuations are fast, power broadening, etc. We show that the \( Q \) parameter exhibits rich types of behaviors, in particular, it reveals the quantum nature of the emission process in the sub-Poissonian regime, while the corresponding model line shape exhibits a classical behavior. A brief summary of our results was recently published.

Here we obtain analytical expressions for \( Q \), and classify the transitions between sub- and super-Poissonian statistics. They give the conditions on the spectral diffusion time scale for sub-Poissonian behavior. Motional narrowing type of effect is revealed for the \( Q \) parameter. Our exact result is valid for weak and strong excitation (i.e., arbitrary Rabi frequency). It yields the lower bound on \( Q \). The solution shows how we may choose the Rabi frequency so that the quantum nature of the photon emission process becomes larger, namely, how to minimize \( Q \) in the sub-Poissonian regime. This is important for the efficient detection of quantum effects in single molecule spectroscopy, since choosing too small or too large values of the Rabi frequency results in very small and hence undetectable values of \( Q \).

### II. INTRODUCTION TO SUB-POISSONIAN STATISTICS

We briefly explain some of the main ideas of sub-Poissonian statistics. The general idea is that the photons emitted from a single particle, e.g., a molecule, a nanocrystal, or atom, are correlated in time. Consider first a hypothetical molecule, interacting with an exciting laser field, which emits photons with a constant time interval \( \tau \) between successive emission events. Then \( \bar{N} = t/\tau, \bar{N}^2 = \bar{N}^2 \), and hence \( Q = -1 \). Due to quantum uncertainty the photon emission process is always random and therefore \( -1 < Q \). Sub-Poissonian behavior where \( -1 < Q < 0 \) implies that the stream of photons emitted from a single source maintain correlations in their arrival times to a detector.

Usually when many molecules interact with a continuous wave laser the emission events are not correlated and the fluorescence exhibits Poissonian statistics, \( Q = 0 \). In contrast a single molecule, once it emits a photon, is collapsed to its ground state. Hence immediately after an emission event the molecule cannot emit a second time (it has to be reexcited by the laser). Hence successive photons emitted from a single molecule seem to repel each other on the time axis, a non-Poissonian behavior. This well-known effect is called antibunching which is related to sub-Poissonian statistics.

A second effect related to sub-Poissonian behavior is Rabi oscillations. Consider a simple atom in the process of resonance fluorescence. When the electronic transition (frequency \( \omega_0 \)) is in resonance with a continuous wave laser field (frequency \( \omega_L \)) the electronic transition can be approximated by a two level system. First let us mentally switch off the spontaneous emission, i.e., set the inverse lifetime of the transition \( \Gamma = 0 \). For zero detuning, \( \omega_L = \omega_0 \), the transition will exhibit well-known Rabi oscillations; the population of the excited state will behave like \( \rho_{ee} = \sin^2(\Omega t/2) \) where \( \Omega \) is the Rabi frequency. Since the population in the excited state attains its maximum (minimum) periodically, also the emission times of successive photons maintain certain degree of periodicity in time, which implies sub-Poissonian statistics. Mandel showed that for a two level atom in the process of resonance fluorescence

\[
Q = -\frac{6\Omega^2\Gamma^2}{(\Gamma^2 + 2\Omega^2)^2}.
\]

When \( \Omega \ll \Gamma \) we have \( Q \to 0 \) since then successive photon emission times are not correlated, because the time between successive emissions becomes very large, while when \( \Omega \gg \Gamma \) the excited state is populated swiftly and only the finite spontaneous emission rate delays the emission, hence \( Q \to 0 \) also in this case. Using Eq. (2) the lower bound \( Q \geq -3/4 \) is easily obtained, and the minimum \( Q_{\text{min}} = -3/4 \) is obtained when \( \Omega_{\text{min}} = \Gamma / \sqrt{2} \).

### III. MODEL AND GENERATING FUNCTION

**FORMALISM**

In this section we briefly review the generating function formalism and present tools needed for obtaining the exact solution in Sec. IV.

Let \( N \) be the random number of photons emitted by a single molecule source in a time interval \((0, t)\) and \( P_N(t) \) be the probability of \( N \) emission events. The information about the photon statistics is contained in the moment generating function

\[
2 \tilde{\gamma}(s) = \sum_{N=0}^{\infty} s^N P_N(t),
\]
which yields the moments of $N$,
\[
\overline{N(t)} = 2N(1), \quad \overline{N^2(t)} = 2\overline{N(1)} + 2N(1),
\]
with which the $Q$ parameter can, in principle, be obtained. In Eq. (4), and in what follows, we use the notation
\[
\frac{\partial}{\partial s} g(s) \bigg|_{s=1} = g'(1)
\]
and similarly for second-order derivatives with respect to $s$. The overline in Eq. (4) describes an average over the process of photon emission; later we will consider a second type of average with respect to the spectral diffusion process, which we will denote with $\langle \cdot \rangle$.

The equations of motion for the generating function was given in Ref. 42 and are called generalized optical Bloch equations. For a chromophore with single excited and ground states, and interacting with a continuous wave laser field,
\[
\dot{\mathcal{U}}(s) = -\frac{\Gamma}{2}\mathcal{U}(s) + \delta_L(t)\mathcal{V}(s),
\]
\[
\dot{\mathcal{V}}(s) = -\delta_L(t)\mathcal{U}(s) - \frac{\Gamma}{2}\mathcal{V}(s) - \Omega\mathcal{W}(s),
\]
\[
\dot{\mathcal{W}}(s) = \Omega\mathcal{V}(s) - \frac{\Gamma}{2}(1+s)\mathcal{W}(s) - \frac{\Gamma}{2}(1+s)\mathcal{Y}(s),
\]
\[
\dot{\mathcal{Y}}(s) = -\frac{\Gamma}{2}(1-s)\mathcal{V}(s) - \frac{\Gamma}{2}(1-s)\mathcal{Y}(s).
\]
These equations are exact within the rotating wave approximation and optical Bloch equation formalism. They yield the same type of information on photon statistics contained in the quantum jump approach to quantum optics which is used in quantum Monte Carlo simulations.\(^{30,48}\) In Eq. (6) $\Gamma$ is the spontaneous emission rate of the electronic transition and $\Omega$ is the Rabi frequency. The time evolving detuning is
\[
\delta_L(t) = \omega_L - \omega_0 - \Delta\omega(t),
\]
where $\omega_L$ ($\omega_0$) is the laser frequency (the molecule’s bare frequency) and $\Delta\omega(t)$ is the stochastic spectral diffusion process. In Eq. (6) it is assumed that the molecules in its excited and ground states have no permanent dipole moments, hence the system is described only by the transition dipole moment via the Rabi frequency.

The physical meaning of $\mathcal{U}(s)$, $\mathcal{V}(s)$, and $\mathcal{W}(s)$ and their relation to the standard Bloch equation was given in Ref. 42, some discussion on this issue will follow Eq. (10). For related work on the foundations of these equations see Refs. 49 and 50, and references therein. Note that when $s \to 1$ the damping terms in Eq. (6) become small [i.e., the $(1-s)\Gamma/2$ terms], hence relaxation of the generalized Bloch equations in the important limit of $s \to 1$ is slow.

In what follows we will consider the moments $\overline{N(t)}$ and $\overline{N^2(t)}$. For this aim it is useful to derive equations of motion for the vector
\[
z = \{\mathcal{U}(1), \mathcal{V}(1), \mathcal{W}(1), \mathcal{Y}(1), \mathcal{U}'(1), \mathcal{V}'(1), \mathcal{W}'(1), \mathcal{Y}'(1)\}\]  
\[
\mathcal{Y}'(1), \mathcal{Y}''(1), \mathcal{Y}''(1)\},
\]
Taking the first and the second derivative of Eq. (6) with respect to $s$ and setting $s=1$, we find
\[
\dot{z} = M(t)z,
\]
where $M(t)$ is a $9 \times 9$ matrix given by
\[
M(t) = \begin{pmatrix}
-\frac{\Gamma}{2} & \delta_L(t) & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\delta_L(t) & -\frac{\Gamma}{2} - \Omega & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \Omega & -\gamma & -\gamma & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \gamma & \gamma & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\delta_L(t) & -\frac{\Gamma}{2} - \Omega & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\gamma & -\gamma & \Omega & \gamma & 0 & 0 \\
0 & 0 & \gamma & \gamma & 0 & 0 & \Omega & \gamma & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \gamma & \gamma & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \gamma & \gamma
\end{pmatrix}.
\]
The first three lines of $M(t)$ describe the evolution of $\mathcal{U}(1)$, $\mathcal{V}(1)$, $\mathcal{W}(1)$, these are the standard optical Bloch equations in the rotating wave approximation.\cite{22,26} These equations yield $\mathcal{W}(1)$ which in turn gives the mean number of photons using Eq. (4),

$$\hat{N}(t) = \Gamma [\mathcal{W}(1) + \frac{1}{2}],$$

(11)

and as usual $\mathcal{W}(1)+\frac{1}{2}$ is the population in the excited state. The fourth line of $M(t)$ is zero, it yields $\hat{\mathcal{Y}}(1)=0$, this equation describes the normalization condition of the problem, namely, $\mathcal{Y}(1)=1/2$ for all times $t$ [to see this use Eq. (3) and $\Sigma_{N=0}P_N(t)=1$]. The evolutions of the other terms $\mathcal{U}'(1)$, $\mathcal{V}'(1)$, $\mathcal{W}'(1)$, $\mathcal{Y}'(1)$ are of current interest since they describe the fluctuation of the photon emission process. In particular, using Eqs. (4) and (10), we obtain

$$\frac{d}{dt}[\hat{N}(t)[N(t)-1]] = \Gamma [\hat{N}(t) + 2\mathcal{W}(1)].$$

(12)

Solutions of time dependent equations like Eq. (9) are generally difficult to obtain, a formal solution is given in terms of the time ordering operator $T$, $z(t)=T \exp[\int_0^t M(t)dt]z(0)$.

Equation (9) yields a general method for the calculation of $Q$ for a single molecule undergoing a stochastic diffusion process. The aim of this paper is to obtain an exact solution of the problem for an important stochastic process used by Kubo and Anderson\cite{44,51,52} to investigate characteristic behaviors of the line shapes. We assume $\Delta \omega(t)=\nu h(t)$ where $\nu$ describes frequency shifts and $h(t)$ describes a random telegraph process: $h(t)=1$ or $h(t)=-1$. The transition rate between state up (+) and state down (−) and vice versa is $R$. This dichotomic process is sometimes called the Kubo–Anderson process.\cite{53} It was used to describe generic behaviors of line shapes,\cite{22,26,54} here our aim is to calculate $Q$ describing the line shape fluctuations.

We use Burshtein’s method\cite{55,56} of marginal averages to solve the stochastic differential matrix equation (9). The method yields the average $\langle z \rangle$ with respect to the stochastic process. We will calculate $\langle z \rangle$ in the limit of long times and then obtain the steady state behavior of the line shape

$$I(\omega_L) = \lim_{t \to \infty} \frac{d}{dt} \langle \hat{N}(t) \rangle$$

(13)

and the $Q$ parameter. Let $\langle z \rangle$ be the average of $z(t)$ under the condition that at time $t$ the value of $h(t) = \pm 1$, respectively. $\langle z \rangle$ are called marginal averages, the complete average is $\langle z \rangle=\langle z \rangle_+ + \langle z \rangle_-$. The equation of motion for the marginal averages is an $18 \times 18$ matrix equation\cite{11} [see also Eq. (A2) of Ref. 26],

$$\begin{pmatrix} \langle z_+ \rangle \\ \langle z_- \rangle \end{pmatrix} = \begin{pmatrix} M_+ - RI & RI \\ RI & M_- - RI \end{pmatrix} \begin{pmatrix} ⟨z_+⟩ \\ ⟨z_-⟩ \end{pmatrix}.$$  

(14)

In Eq. (14) the matrix $M_\pm$ is identical to matrix $M$ in Eq. (10) when $\delta_L(t)$ is replaced by $\delta_L = \omega_L - \omega_0 + \nu$ and $I$ is a $9 \times 9$ identity matrix. In the following section we obtain the long time solution of Eq. (14), the reader not interested in the mathematical details may skip to Sec. IV A, where the solution for the line shape and $Q$ is presented.

IV. MATHEMATICAL DERIVATION OF EXACT SOLUTION

In three main steps, we now find the long time behavior of the marginal averages, with which the line and $Q$ are then obtained.

(1) As mentioned, from normalization condition we have $\mathcal{Y}(1)=1/2$ for all times. Equation (14) yields the marginal averages $\langle \mathcal{Y}(1) \rangle = (\langle \mathcal{Y}(1) \rangle_+ = 1/4$ in the steady state. Inserting these identities in Eq. (14) we obtain an equation of motion for the vector

$$y = \langle \{ \mathcal{U}(1)_+, \mathcal{V}(1)_+, \mathcal{W}(1)_+, U(1)_-, \mathcal{V}(1)_-, \mathcal{W}(1)_- \} \rangle,$$

(15)

$$\dot{y} = Ay + b_0,$$

(16)

where

$$A = \begin{pmatrix} \frac{\Gamma}{2} - R & \delta_L & 0 & R & 0 & 0 \\ -\delta_L & -\frac{\Gamma}{2} - R & -\Omega & 0 & R & 0 \\ 0 & \Omega & -\Gamma - R & 0 & 0 & R \\ R & 0 & 0 & \frac{\Gamma}{2} - R & \delta_L & 0 \\ 0 & R & 0 & -\delta_L & -\frac{\Gamma}{2} - R & -\Omega \\ 0 & 0 & R & \Omega & -\Gamma - R \end{pmatrix}.$$ 

(17)
and \( b_0 = (0, 0, -\Gamma/4, 0, 0, -\Gamma/4) \). In the long time limit the solution of Eq. (16) reaches a steady state (ss) given by
\[
y^{ss} = -A^{-1}b_0
\] (18)
and \( A^{-1} \) is the inverse of \( A \). From Eq. (18) we find that
\[
\langle W^{ss}(1) \rangle_+ = \frac{\Gamma}{4} (A_{33}^{-1} + A_{36}^{-1}),(19)
\]
\[
\langle W^{ss}(1) \rangle_- = \frac{\Gamma}{4} (A_{63}^{-1} + A_{66}^{-1})
\]
where \( A_{ij}^{-1} = A_{ji}^{-1} \) and \( A_{ij}^{-1} \) is the \( ij \) matrix element of \( A^{-1} \), \( i, j = 1, \ldots, 6 \). We note that \( \langle W^{ss}(1) \rangle_\pm \) yields the steady state marginal averages of the population difference between the excited and ground states. From Eq. (4) we see that we need \( 2\langle \mathcal{Y}(1) \rangle \) to obtain the average number of photon emissions \( \langle \mathcal{N} \rangle \). We use Eq. (14) and show
\[
\langle \mathcal{Y}^{ss}(1) \rangle = \langle \mathcal{Y}^{ss}(1) \rangle_+ + \langle \mathcal{Y}^{ss}(1) \rangle_-
= \frac{\Gamma}{2} \left( \langle W^{ss}(1) \rangle_+ + \langle W^{ss}(1) \rangle_- + \frac{1}{2} \right) t
\] (20)
and
\[
\langle \mathcal{Y}^{ss}(1) \rangle_+ - \langle \mathcal{Y}^{ss}(1) \rangle_- = \frac{\Gamma \langle \langle W^{ss}(1) \rangle_+ - \langle W^{ss}(1) \rangle_- \rangle}{4R}.
\] (21)
The average number of emitted photon, in the long time limit is (4) and (20)
\[
\langle \mathcal{N} \rangle = \Gamma \left( \langle \mathcal{Y}^{ss}(1) \rangle_+ + \langle \mathcal{Y}^{ss}(1) \rangle_- + \frac{1}{2} \right) t,
\] (22)
namely, \( \langle \mathcal{N} \rangle \) is proportional to the steady state occupation in the excited state. The line shape is
\[
I(\omega_r) = I_+ + I_- = \frac{I_+ + I_-}{2},
\] (23)
where
\[
I_\pm = \frac{\Gamma^2}{2} \left[ \langle W^{ss}(1) \rangle_\pm + \frac{1}{2} \right].
\] (24)

(2) We use the solutions obtained in previous step to obtain inhomogeneous equations for \( x = (\mathcal{U}(1)_+, \mathcal{Y}(1)_+, \mathcal{Y'}(1)_+, \mathcal{V}(1)_+, \mathcal{V'}(1)_-, \mathcal{W}(1)_-, \mathcal{W'}(1)_-) \),
\[
\dot{x} = Ax + b(t),
\] (25)
where \( b(t) = [0, 0, b_1(t), 0, 0, b_2(t)] \) with
\[
\begin{align*}
b_1(t) &= \frac{\Gamma}{8} \left( \langle W^{ss}(1) \rangle_+ - \langle W^{ss}(1) \rangle_- \right) - \frac{\Gamma^2}{8} \left( 1 + 2[\langle W^{ss}(1) \rangle_+ + \langle W^{ss}(1) \rangle_-] \right) \\
&= \frac{\Gamma^2}{8R} \left( \langle W^{ss}(1) \rangle_- - \langle W^{ss}(1) \rangle_+ \right),
\end{align*}
\] (26)
In the long time limit we obtain
\[
x(t) \sim A^{-1}c_0 + (A^{-1}t + A^{-1}A^{-1})c_1,
\] (27)
where \( c_0 \) and \( c_1 \) are column vectors,
\[
c_0 = (0, 0, c_+, 0, 0, c_-), \quad c_1 = \left( 0, 0, \frac{\Gamma I(\omega_r)}{4}, 0, 0, \frac{\Gamma I(\omega_r)}{4} \right),
\] (28)
with
\[
c_\pm = \frac{\Gamma}{2} \left[ \langle W^{ss}(1) \rangle_\pm + \frac{1}{4} \right] \mp \frac{\Gamma^2}{8R} \left( \langle W^{ss}(1) \rangle_- - \langle W^{ss}(1) \rangle_+ \right).
\] (29)
We therefore obtain
\[
\langle W^{ss}(1) \rangle_+ = A_{33}^{-1}c_+ + A_{36}^{-1}c_- + I(\omega_r) \langle W^{ss}(1) \rangle_t
+ \frac{\Gamma I(\omega_r)}{4} \left[ \langle A^{-1}A^{-1} \rangle_{33} + \langle A^{-1}A^{-1} \rangle_{36} \right],
\] (30)
\[
\langle W^{ss}(1) \rangle_- = A_{63}^{-1}c_+ + A_{66}^{-1}c_- + I(\omega_r) \langle W^{ss}(1) \rangle_t
+ \frac{\Gamma I(\omega_r)}{4} \left[ \langle A^{-1}A^{-1} \rangle_{63} + \langle A^{-1}A^{-1} \rangle_{66} \right],
\] (31)
(3) From Eq. (4), \( \langle \mathcal{N}(t) \rangle = \langle \mathcal{Y}(1) \rangle + \langle \mathcal{Y'}(1) \rangle \). In steady state we have
\[
\langle \mathcal{Y}(1) \rangle = \langle \mathcal{Y}(1) \rangle_+ + \langle \mathcal{Y}(1) \rangle_-
\] (32)
From Eq. (14) one can show that in the long time limit
\[
\langle \mathcal{Y}(1) \rangle = 4 \left[ \langle W^{ss}(1) \rangle_+ c_+ + \langle W^{ss}(1) \rangle_- c_- \right] t
+ \frac{\Gamma I(\omega_r)}{4} \left[ \langle A^{-1}A^{-1} \rangle_{33} + \langle A^{-1}A^{-1} \rangle_{36} \right] t
+ \langle A^{-1}A^{-1} \rangle_{63} + \langle A^{-1}A^{-1} \rangle_{66} \right] t
\] (33)
Finally we obtain the \( Q \) parameter using
\[
Q = \frac{\langle \mathcal{Y}(1) \rangle^2 - 2 \langle \mathcal{Y}(1) \rangle^2}{\langle \mathcal{Y}(1) \rangle^2}.
\] (34)
Using Eqs. (20), (33), and (34) we obtain the main result of this paper,
\[
Q = \frac{\Gamma^2}{2} \sum_{i=3,6} \sum_{j=3,6} (A^{-1}A^{-1})_{ij}
+ \frac{\Gamma^2 I(\omega_r)}{R} \left[ \langle W^{ss}(1) \rangle_+ - \langle W^{ss}(1) \rangle_- \right]^2
+ \frac{1}{I(\omega_r)} \sum_{k=2} \left( \langle W^{ss}(1) \rangle_k \left[ 1 + 4 \langle W^{ss}(1) \rangle_k \right] \right),
\] (35)
which is valid when measurement time \( t \to \infty \). The \( Q \) parameter in Eq. (35) is expressed in terms of \( A^{-1} \). To obtain the solution in terms of the original parameters of the problem \( R, \nu, \omega_r, \omega_0, \Omega, \Gamma \), we found analytical expressions for \( A^{-1} \) using MATHEMATICA. The formula for the \( Q \) parameter is given in the following section.
A. Exact solution

Without loss of generality we set \( \omega_0 = 0 \), hence \( \omega_L \) is the detuning. We find

\[
Q = \frac{\text{Numerator}[Q]}{\text{Denominator}[Q]}. 
\]

Numerator\([Q]\) = \(-2\Gamma\Omega^2(R(\Gamma + 4R)(3\Gamma^3 - 4\Gamma^2 + 24\Gamma^2R + 16\nu^2R + 48\Gamma^2R^2)[3\Gamma^3 + 6\Gamma^2R + 8\nu^2R + 2\Gamma(2\nu^2 + \Omega^2 + 4R^2)]^3 + 8(4\Gamma^3R - 4\Gamma^2[\nu^2 - 21\Gamma^2R^2] - 3072\Gamma^2[\nu^2R^2(4\nu^2 - \Omega^2 - 16R^2) - 4096\nu^2R^2(2\nu^2 - \Omega^2 - 4R^2) + 15\Gamma^2R(\Omega^2 + 4R^2) - 81[4\nu^2 - 27\Gamma^2R^2 - 392R^4 + 2\nu^2(\Omega^2 - 48R^2)] - 4\Gamma^2R(128R^6 + \Omega^6 + 48\Gamma^2R^2 + 1344\Omega^2R^4 + 64000R^6 + 112\Omega^2 - 272R^2 + 4\nu^2(9\Omega^4 - 302\Omega^2R^2 - 5072R^4)] - 64\Gamma^3R[48\nu^2 + 3\nu^2(11\Omega^2 - 44R^2) + 3(\Omega^2 + 4R^2)^3(\Omega^2 + 16R^2) + 2\nu^2(5\Omega^4 - 80\Omega^2R^2 - 544R^4)] - 256\Gamma^3R^2[28\nu^2 + \nu^2(3\Omega^2 - 32\Omega^2R^2 + (\Omega^2 + 4R^2)^2) + 2\nu^2(\Omega^4 - 4\Omega^2R^2 - 32R^4)] + 4\Gamma^2R(- 48\nu^2 - 2\nu^2(9\Omega^2 - 952R^2) + 3(\Omega^4 + 89\Omega^2R^2 + 544R^4)] - 8\Gamma^6[8\nu^2 + 8\nu^2(\Omega^2 - 17\Omega^2) + 2\nu^2(\Omega^2 - 38\Omega^2R^2 - 2116R^4) - 3(3\Omega^2R^2 + 58\Omega^2R^4 + 40\nu^2R^2) - 161\nu^4R^2[96\nu^4 + 96\nu^2(\Omega^2 - 31\Omega^2) + 2\nu^2(26\Omega^2 - 720\Omega^2R^2 - 6656R^4)] + 3(\Omega^2 + 44\Omega^2R^2 + 448\Omega^2R^4 + 1152\Gamma^2R^4)]\)^2 + 32(\Gamma + 2R)(3\Gamma^3R + 512\Gamma^2R^4 + 512\nu^2R^4 - 81\nu^2(\nu^2 - 3R^2) + \Gamma^2[-32\nu^2R + 3(\Omega^2 - 4R^2)] - 32\nu^2R[-14\nu^2 + 6\nu^2R^2 + 3(\Omega^2 + 4R^2)^2]) + 2\Gamma^5[16\nu^2 - 8\nu^2(\Omega^2 - 3R^2) - 3R^2(5\Omega^2 + 104R^4)] - 8\Gamma^3R[-56\nu^2 + \nu^2(29\Omega^2 - 40R^2) + 6(\Omega^4 + 20\Omega^2R^2 + 64R^4)] - 2\Gamma^4R[-104\nu^2 + 10\nu^2(5\Omega^2 - 16R^2) + 3(\Omega^4 + 60\Omega^2R^2 + 368R^4)]\)^2 - 128\Gamma^2(\Gamma + 2R)^2(4\nu^2 + 3R^2) + \Gamma R(16\nu^2 + 3\Omega^2 - 48R^2) + 4\Gamma^4[4\nu^2 + 3(\Omega^2 + 4R^2)^2]\)^2 - 256\Gamma^2(\Gamma + 2R)(3\Gamma^2R^4 + 2\nu^2R^2 + 2\nu^2(\Omega^2 - 8\Omega^2R^2 + 6\Omega^2R^4 + 16R^2) + 2\nu^2(\Omega^2 + 8R^2)) + 16\Gamma(\Gamma + 2R)\)^2. 

Denominator\([Q]\) = \(R((\Gamma + 4R)[3\Gamma^3 + 6\Gamma^2R + 8\nu^2R + 2\Gamma(2\nu^2 + \Omega^2 + 4R^2)] + 4\Gamma(\Gamma + 2R)\omega_L^2[\nu^2 + 10\Gamma^2R + 64\nu^2\Gamma^2R^2 - 4\Gamma^4(2\nu^2 + \Omega^2 + 8R^2) + 4\Gamma^3R(12\nu^2 + 7\Omega^2 + 8R^2) + 16\Gamma R(2\nu^2 + 3\nu^2\Omega^2 + \Omega^4 + 4\Omega^2R^2) + 4\Gamma^2[4\nu^2 + \Omega^4 + 16\nu^2R^2 + 4\nu^2(\Omega^2 + 4R^2)] + 8\Gamma[3\Gamma^3 + 6\Gamma^2R - 8\nu^2R + 6\Omega^2R + 16\nu^2R + 16R^3 + 2\Gamma(-2\nu^2 + \Omega^2 + 8R^2)]\omega_L^2 + 16\Gamma(\Gamma + 2R)\omega_L^2)^2. 

The line shape is

\[
I(\omega_L) = \frac{\text{Numerator}[I(\omega_L)]}{\text{Denominator}[I(\omega_L)]}. 
\]

Numerator\([I(\omega_L)]\) = \(\Gamma\Omega^2((\Gamma + 4R)[3\Gamma^3 + 6\Gamma^2R + 8\nu^2R + 2\Gamma(2\nu^2 + \Omega^2 + 4R^2)] + 4\Gamma(\Gamma + 2R)\omega_L^2\)^2.

Denominator\([I(\omega_L)]\) = \(\Gamma^6 + 10\Gamma^3R + 64\nu^2\Omega^2R^2 + 4\nu^2(2\nu^2 + \Omega^2 + 8R^2) + 4\Gamma^3R(12\nu^2 + 7\Omega^2 + 8R^2) + 16\Gamma R(2\nu^2 + 3\nu^2\Omega^2 + \Omega^4 + 4\Omega^2R^2) + 4\Gamma^2[4\nu^2 + \Omega^4 + 16\nu^2R^2 + 4\nu^2(\Omega^2 + 4R^2)] + 8\Gamma[3\Gamma^3 + 6\Gamma^2R - 8\nu^2R + 6\Omega^2R + 16\nu^2R + 16R^3 + 2\Gamma(-2\nu^2 + \Omega^2 + 8R^2)]\omega_L^2 + 16\Gamma(\Gamma + 2R)\omega_L^2\)^2.

1. Exact solution for zero detuning

When the detuning is zero we find that

\[
Q(\omega_L = 0) = -\frac{2\Gamma\Omega^2[4\nu^2(-\Gamma + 4R) + 3\Gamma(\Gamma + 4R)]}{[4\Gamma^2(2\nu^2 + (\Gamma^2 + 2\nu^2)(\Gamma + 4R)^2]}. 
\]

Using Eq. (38) the lower bound \(Q(\omega_L = 0) > -3/4\) is obtained. The absolute minimum of \(Q\), i.e., \(Q = -3/4\) is found when \(\nu = 0, \Omega = \sqrt{1/2}\) or when \(R \to \infty, \Omega = \sqrt{1/2}\). Namely, the absolute minimum is found for a molecule whose absorption frequency is fixed or for a very fast spectral modulation.

Remark. Equation (38) indicates a transition from sub-Poissonian statistics \(Q < 0\) to super-Poissonian statistics \(Q > 0\) when \(4\nu^2 = 3(\Gamma + 4R^2)/(\Gamma - 4R)\). If \(R > \Gamma/4\), i.e., if the bath is fast compared with the radiative lifetime, we find sub-Poissonian behavior for all values of \(\nu\) and \(\Omega\).

V. THE PHYSICAL BEHAVIORS OF THE EXACT SOLUTION IN LIMITING CASES

The \(Q\) parameter is a function of two control parameters \(\omega_L\) and \(\Omega\), and three model parameters \(\Gamma, R, \nu\). The classification of different types of physical behaviors based on the
A. Slow modulation regime: $R \ll \nu, \Gamma, \Omega$

In the slow modulation regime, the bath fluctuation rate $R$ is small compared with the radiative decay rate $\Gamma$, frequency fluctuation amplitude $\nu$, and the Rabi frequency $\Omega$. This case is similar to situations in many single molecule experiments, for example, single molecules in low temperature glasses.

The exact solution can be simplified in the limit $R \to 0$, using Eq. (37),

$$\lim_{R \to 0} I(\omega_L) = \frac{I_+(\omega_L) + I_-(\omega_L)}{2},$$

(39)

and

$$I_\delta(\omega_L) = \frac{\Gamma \Omega^2}{[\Gamma^2 + 2\Omega^2 + 4(\omega_L \mp \nu)^2]}.$$

(40)

The line is a sum of two Lorentzians centered on $\pm \nu$, namely, it exhibits splitting behavior when $\nu \gg \Gamma, \Omega$. Using Eq. (36) we find a simple super-Poissonian behavior for $Q$ in the slow modulation limit $R \to 0$,

$$Q \sim Q_{\text{slow}} = \frac{(I_+ - I_-)^2}{4RI},$$

(41)

and since $R \to 0$, $Q$ may become very large (e.g., $Q=5 \times 10^6$ in Fig. 1).

A simple picture can be used to understand these results. In the slow modulation limit the molecule jumps between two states $+\,\ddagger\, -\,\ddagger\, \ddagger\, -\,\ddagger\,$, the time between successive jumps is very long, in such a way that many photons are emitted between jump events. In each of these two states the molecule emits photons at a rate $I_\delta(\omega_L)$, Eq. (40). These rates are determined by the familiar steady state solutions of the optical Bloch equation, for a two level atom with the absorption frequency $\omega_0 \pm \nu$ fixed in time. In this slow limit the random number of emitted photons, in time interval $(0, t)$, is $N_{\text{slow}} = \int_0^t I(\omega_L) d\omega_L$ and $I(\omega_L)$ is a stochastic intensity that jumps between two states $I_\delta(\omega_L)$ with the rate $R$. Using this simple random walk picture it is straightforward to derive Eqs. (39) and (41). For mathematical details see Ref. 26 which considered a similar slow modulation limit which is valid only for weak Rabi frequency.

1. $R \ll \Gamma, \Omega \ll \nu$

Within the slow modulation limit we distinguish between two cases. The case $R \ll \Gamma, \Omega \ll \nu$ is called the slow modulation strong coupling limit. In this case the line and $Q$ have two well-separated peaks and the broadening of the two peaks due to the finite lifetime and power of the laser field is small compared with the frequency shifts (see Fig. 1). From Fig. 1, and as expected from Eqs. (39) and (41), $Q$ decreases when $R$ is increased, while $I(\omega_L)$ is independent of $R$. Thus it is $Q$ not $I(\omega_L)$ that yields information on the dynamics. In Fig. 1 the agreement between the exact solution and the approximation Eq. (41) is good.

2. $R \ll \nu, \Gamma = \Omega$

The limit $R \ll \nu, \Gamma = \Omega$ is called the weak coupling slow modulation limit. In this case the two peaks of the line, discussed in the preceding section, are overlapping and the line is approximated by

$$I(\omega_L) \sim \frac{\Gamma \Omega^2}{\Gamma^2 + 2\Omega^2 + 4\omega_L^2}.$$

(42)

This result is exact when $\nu=0$ for arbitrary $R$.

The behavior of $Q$ is demonstrated in Fig. 2, where we observe both super-Poissonian and sub-Poissonian behaviors. In the slow modulation weak coupling limit, we must distinguish between the cases of large and small detuning. First note that according to Eq. (41) when the detuning is zero we find $Q=0$, namely, the leading $1/R$ term in our asymptotic expansion vanishes. We must therefore consider the higher order terms in our asymptotic expansion of Eq. (36) and we find

$$Q \sim Q_{\text{slow}} + Q_M,$$

(43)

where
FIG. 2. Same as Fig. 1 for the slow modulation weak coupling case $R \ll \nu \ll \Gamma = \Omega$. We see that the line $I$ is Lorentzian in shape while the $Q$ parameter exhibits splitting. And unlike the line shape $Q$ depends on $R$ in this limit. In the vicinity of zero detuning $Q$ exhibits a sub-Poissonian behavior ($Q < 0$). Far from zero detuning the slow spectral diffusion process controls the behavior of $Q$ and then $Q > 0$. The asterisks (*) are the approximate equations for $Q$, Eq. (45), and $I$, Eq. (42). The parameters are $\Gamma = 40$ MHz, $\nu = \Gamma / 10$, $\Omega = \Gamma / \sqrt{2}$, and $R = \Gamma / 2500$ (solid curve), $\Gamma / 500$ (dashed-dot curve), and $\Gamma / 100$ (dashed curve).

$$Q_M = -\frac{2\Omega^2(3\Gamma^2 - 4\omega_d^2)}{(\Gamma^2 + 2\Omega^2 + 4\omega_d^2)^2}.$$  (44)

Equation (43) has a simple meaning, the first term is a contribution to $Q$ from spectral diffusion, which is identical to Eq. (41). The second term $Q_M$ is identical to the result obtained by Mandel, for the $Q$ parameter in the absence of spectral diffusion, $^{31}$ and $Q_M < 0$ provided that the detuning is not too large. The second term is dominating over the first when the detuning is small, and for zero detuning we obtain in Eq. (43) sub-Poissonian statistics. More explicitly, we Taylor expand Eq. (40) using $\nu$ as a small parameter and obtain for the slow modulation weak coupling limit

$$Q = \frac{64\Gamma^2\omega_d^2\nu^2}{R(\Gamma^2 + 2\Omega^2 + 4\omega_d^2)^3} \cdot \frac{2\Omega^2(3\Gamma^2 - 4\omega_d^2)}{(\Gamma^2 + 2\Omega^2 + 4\omega_d^2)^2}. $$  (45)

One may say that for zero detuning, the molecule behaves as if its absorption frequency is fixed.

To conclude, we see that in the slow modulation limit $Q$ is a sum of two additive contributions: (i) a part related to spectral diffusion $Q_{s\text{low}}$ and (ii) a part related to quantum fluctuations, i.e., $Q_M$. The quantum fluctuations are bounded from below $-3/4 < Q_M$, while for the spectral diffusion contribution we have $0 < Q_{s\text{low}} < \infty$. Hence detection of the quantum fluctuations is possible only when $Q_{s\text{low}}$ is small, which for our case implies zero detuning and weak coupling limit. After our work was completed, and partly published in Ref. 40, an approximation scheme to the slow modulation limit was obtained in Ref. 43 which yields behaviors similar to our exact results (see also Ref. 26 for related discussion).

B. Fast modulation regime: $R \gg \nu, \Gamma, \Omega$

We now consider the fast modulation limit. If we take $R \rightarrow \infty$ keeping $\Omega$, $\Gamma$, and $\nu$ fixed we find from Eq. (36),

$$\lim_{R \to \infty} Q = Q_M$$  (46)

given in Eq. (44). Hence in this limit we find a sub-Poissonian behavior, provided that the detuning $\omega_d$ is not too large. The line shape is identical to the expression on the right-hand side of Eq. (42). This behavior is expected; when the spectral diffusion is very fast the emitting single molecule cannot respond to the stochastic fluctuations.

A more interesting case is to let $R \rightarrow \infty$ and $\nu \rightarrow \infty$ but keep...
\[ \Gamma_{SD} = \frac{v^2}{R} \]  

finite. We call this limit the fast modulation limit; using Eq. (37) the line shape is

\[ I_{fast}(\omega) = \frac{(\Gamma + \Gamma_{SD})\Omega^2}{(\Gamma_{SD} + \Gamma)^2 + 2(1 + \Gamma_{SD}/\Gamma)\Omega^2 + 4\omega_L^2}, \]  

and when the Rabi frequency is small

\[ 2\Gamma\Omega^2\left[3\Gamma^3 + 5\Gamma^2\Omega + \Gamma^2 - 4\Gamma\omega_L^2 + \Gamma_{SD}(7\Gamma^2 + 4\omega_L^2)\right] 
\[ \Gamma^3 + \Gamma^2\Omega^2 + 2\Gamma\Omega^2 + 2\Gamma_{SD}(\Gamma^2 + \Omega^2) + 4\Gamma\omega_L^2 \]  

Thus in the fast modulation limit the photon statistics is sub-Poissonian provided that the detuning is not too large. When \( \Gamma_{SD} \to 0 \) the result for \( Q \) reduces to Mandel’s result, Eq. (44).

In Fig. 3, we show the line shape and the \( Q \) parameter for three values of the jump rate \( R \) in the fast modulation regime while \( \nu, \Omega, \Gamma \) are kept fixed. We see that as the stochastic spectral diffusion process gets faster, both the line shape and the \( Q \) parameter become narrow. Thus both \( I(\omega) \) and \( Q \) exhibit a motional narrowing effect. Also, as the stochastic process gets faster, a stronger quantum behavior is obtained, in the sense that the minimum of \( Q \) decreases.

C. Strong coupling limit \( \nu \gg R, \Gamma, \Omega \)

To investigate the strong coupling limit we consider the value of \( Q \) for \( \omega_L = \nu \) and \( \nu \gg \Gamma, R, \Omega \). From Eq. (36) we obtain

\[ \lim_{\nu \to \infty} Q_{\omega_L = \nu} = -\frac{(\Gamma + 2R)\Gamma\Omega^2[-\Gamma^3 + 16\Gamma R^2 + 8R^3 - 2\Gamma^2\Omega^2 + 2R(2\Gamma^2 + \Omega^2)]}{2R[(\Gamma^3 + 4\Gamma R^2 + 2\Gamma \Omega^2 + 2R(2\Gamma^2 + \Omega^2))^2]} \]  

This equation exhibits both sub-Poissonian and super-Poissonian behaviors. When the process is very slow, namely, \( R \to 0 \), we obtain

\[ \lim_{\nu \to \infty} Q_{\omega_L = \nu} \sim \frac{\Gamma\Omega^2}{2R(\Gamma^2 + 2\Omega^2)}, \]  

a super-Poissonian behavior. In the intermediate modulation limit, when \( R = \Gamma \), we obtain

\[ \lim_{\nu \to \infty} Q_{\omega_L = \nu} = -\frac{81\Omega^2\Gamma^2}{2(9\Gamma^2 + 4\Omega^2)^2}, \]  

a sub-Poissonian behavior. When \( R \to \infty \) we find that \( Q \) is small,

\[ \lim_{\nu \to \infty} Q_{\omega_L = \nu} \sim -\frac{\Omega^2}{2R}. \]  

Equations (52)–(54) are valid only in the limit of \( \nu \to \infty \). However behaviors similar to the predictions of these equations are found also for finite values of \( \nu \). On \( \omega_L = \nu \) we have three typical behaviors: (i) \( Q(\omega_L = \nu) > 0 \) when the process is slow, see Fig. 1, (ii) \( Q(\omega_L = \nu) < 0 \) when \( \Gamma \approx R \), see Fig. 4 for \( R=\Gamma/2 \), and (iii) when \( R \to \infty \) we find \( Q(\omega_L = \nu) \to 0 \), Fig. 3.

D. Intermediate modulation limit \( R \approx \Gamma \)

When \( R \approx \Gamma \approx \Omega \ll \nu \) we obtain interesting behaviors for \( Q \). In Fig. 4 the \( Q \) parameter shows a transition from sub-Poissonian to super-Poissonian photon statistics. In this regime of parameters, the shape of \( Q \) when plotted as a function of \( \omega_L \) is very sensitive to the value of the control parameters, e.g., in Fig. 4 we change \( R \) only moderately still we see very different types of behaviors for \( Q \). For certain values of parameters \( Q \) attains more than two peaks (see Fig. 4 for \( R=\Gamma/6, \Gamma/4 \)). In contrast \( I(\omega) \) exhibits a simple splitting behavior with two peaks on \( \pm \nu \), which is similar to the slow modulation case.

Besides the transition from sub- to super-Poissonian behavior, a second type of transition is observed as \( R \) is increased. In our problem we have two types of sub-Poissonian behavior. We noticed already that when the stochastic modulation becomes very fast, \( Q \) has one minimum on zero detuning (see Fig. 2), while when \( R \approx \Gamma \), \( Q \) has two minima on \( \omega_L \pm \nu \) (see Fig. 3 and \( R=\Gamma/2 \)). The transition between these two types of sub-Poissonian behaviors is shown in Fig. 5.
VI. EXTREMUM OF Q

We now investigate the dependence of Q on the excitation field. In Fig. 6 we consider an example line shape and Q parameter, where we fix the model parameters ν, R, Γ, and vary the Rabi frequency. For the line we see well-known power broadening: as the Rabi frequency is increased the line becomes wider, and as expected the photon emission rate I(ω/2) increases monotonically when Ω is increased. For the Q parameter we have a turnover behavior, as we increase Ω the value of Q on zero detuning decreases then increases.

Generally this type of turnover is expected, since as discussed in Sec. II, Q=0 when Ω→∞ or Ω→0. Thus there exists an optimal Rabi frequency which yields an extremum of Q. Obviously it is important to obtain the values of Ω which yield the extremum of Q, since then the fluctuations are the largest. The extremum can be either a minimum or a maximum, as we shall show now.

A. Largest quantum fluctuations

We now consider the quantum regime Q<0. In Fig. 7(b) we demonstrate the turnover behavior of Q(Ω) for an example where the stochastic fluctuations are fast. In this fast modulation case Q<0 hence Q(Ω) has a minimum. For the same parameters the photon emission rate I(Ω) increases as Ω is increased, and the emission rate is never faster than Γ [see Fig. 7(a)].

Let Ωmin be the Rabi frequency which minimizes Q in the sub-Poissonian case Q<0, and Qmin the corresponding value of Q. Using Eq. (38) we find for zero detuning and for R>Γ/4

\[ \Omega_{\text{min}} = \sqrt{\frac{\Gamma^3 + 4\Gamma^2 R + 4\Gamma R^2}{2(\Gamma + 4R)}} \]  

(55)

and

\[ Q_{\text{min}} = \frac{-[4\nu^2(-\Gamma + 4R) + 3\Gamma(4R)^2]}{4(\Gamma + 4R)(\Gamma^2 + 4\nu^2 + 4R^2)} . \]  

(56)

Equations (55) and (56) yield Ωmin and Qmin in terms of ν and R. Due to motional narrowing effect, for fast processes satisfying ν≪R, ν and R are not easily obtained from experiment, while the parameter ΓSD is, in principle, easy to obtain from the measurement of the linewidth. Using Eq. (50), we find in the fast modulation limit and for zero detuning

\[ \frac{\Omega_{\text{min}}}{\Gamma} = \sqrt{\frac{1 + \Gamma_{\text{SD}}^2/2}{2}} . \]  

(57)

\[ Q_{\text{min}} = \frac{1 + 3\Gamma_{\text{SD}}}{4(\Gamma + \Gamma_{\text{SD}})} . \]  

(58)

These simple equations relate between the width of the line given in Eq. (49) and Qmin and Ωmin. From Eqs. (57) and (58) we see that when ΓSD≪Γ, Ωmin=Γ/2 and Qmin=−3/4. When ΓSD≫Γ we find Ωmin=ΓSDΓ/2 and Qmin=−1/4.
Remark. When the detuning is not zero, we find using Eq. (50)
\[ \frac{\Omega_{\text{min}}}{\Gamma} = \sqrt{\frac{(1 + \Gamma \delta_{\text{SP}}/\Gamma)^2 + 4 \omega_d/\Gamma^2}{2(1 + \Gamma \delta_{\text{SP}}/\Gamma)}}. \] (59)

Similar turnover behaviors of \( Q(\Omega) \) are found also in other nonfast parameter regimes. In Fig. 8 we show \( Q(\Omega) \) versus \( \Omega \) for the slow modulation weak coupling limit \( R < \nu < \Gamma \) and for zero detuning. Figure 8 shows that \( Q \) exhibits a minimum as function of \( \Omega \); this minimum is found in the vicinity of \( \Omega_{\text{min}} = \Gamma/\sqrt{2} \). Such a behavior is understood based on Eq. (43), the spectral diffusion contribution for \( Q \) is not important at zero detuning, while the contribution of \( Q_M \) yields \( \Omega_{\text{min}} = \Gamma/\sqrt{2} \). To demonstrate that the turnover behavior of \( Q(\Omega) \) is generic, we consider also the intermediate modulation limit in Fig. 9. Here we choose the detuning according to \( \omega_d = \nu \), since the \( Q \) parameter on zero detuning is relatively small (see Fig. 5).

**B. Maximum of super-Poissonian fluctuations**

In contrast to the behaviors in the quantum regime \( Q < 0 \), in the slow modulation limit where \( Q > 0 \), \( Q(\Omega) \) obtains a maximum, whose location is easy to calculate with Eq. (41). Such a behavior is demonstrated in Fig. 10 for a case where the spectral shift \( \nu \) is not very large. If \( \nu \gg \Omega, \Gamma \) then in the slow modulation limit

[FIG. 6. We investigate the dependence the line shape and \( Q \) on the Rabi frequency \( \Omega \). Power broadening of the line is observed, while for the \( Q \) parameter we have a turnover behavior as explained in the text. The three values of the Rabi frequency are \( \Omega = \Gamma/4 \) (dashed curve), \( \Gamma/\sqrt{2} \) (dashed-dot curve), and \( 3\Gamma/2 \) (solid curve). And the minimum of \( Q \), on zero detuning, is obtained for the intermediate value of \( \Omega = \Gamma/\sqrt{2} \). The fixed parameters are \( \Gamma = 40 \text{ MHz}, \nu = 5\Gamma, \) and \( R = 100\Gamma \).

FIG. 7. The photon emission rate \( I(\Omega) \) (a) and the \( Q(\Omega) \) parameter (b) are calculated with the exact solution of Eqs. (37) and (36) in the fast modulation limit. The parameters are \( \Gamma = 40 \text{ MHz}, \nu = 5\Gamma, \omega_d = 0, \Omega = 0 \rightarrow 7\Gamma, \) and \( R = 20\Gamma \). We observe the saturation of the line as \( \Omega \) becomes large while \( Q(\Omega) \) has a minimum. The value of \( \Omega \) which minimizes \( Q(\Omega) \) is of interest since it yields the strongest quantum fluctuations. The symbol \( * \) is the point \( (\Omega_{\text{min}}, Q_{\text{min}}) \) calculated based on the approximation given by Eqs. (57) and (58).

\[ Q_{\text{slow}} = \frac{\Gamma \Omega^2}{2R(\Gamma^2 + 2\Omega^2)} - \frac{3\Gamma \Omega^2}{32R \nu^2} \] (60)

when the detuning is equal to \( \omega_d = \nu \). In Eq. (60) the second term on the right-hand side is supposed to be a correction to the first term, namely, \( Q_{\text{slow}} > 0 \). Let \( \Omega_{\text{max}} \) be the value of \( \Omega \) which maximizes \( Q \) in the super-Poissonian regime, and \( Q_{\text{max}} \) is the corresponding maximum. This maximum always

[FIG. 8. We demonstrate how to choose the Rabi frequency in order to obtain strong sub-Poissonian behavior. The \( Q(\Omega) \) parameter is calculated with the exact solution of Eq. (36). The detuning \( \omega_d = \omega_0 \) is zero, and \( \Gamma = 40 \text{ MHz}, \nu = \Gamma/10 \) and \( R = \Gamma/100 \) correspond to the slow modulation weak coupling limit. The minimum, denoted by the \( * \) in the figure, \( Q_{\text{min}} = -0.71 \) is found for \( \Omega_{\text{min}} = 0.72\Gamma \), which is close to the global minimum \( (Q_{\text{min}}, \Omega_{\text{min}}) = (-3\Gamma, \Gamma/\sqrt{2}) \).]
exists since as mentioned $Q=0$ when $\Omega \to 0$ or $\Omega \to \infty$. Then using Eq. (60)

$$\Omega_{\text{max}} \approx \sqrt{\frac{\Gamma(4\sqrt{3}v - 3\Gamma)}{6}}$$

(61)

which is independent of $R$ and

$$Q_{\text{max}} \approx \frac{\Gamma(3\Gamma^2 + 16v^2 - 8\sqrt{3}\Gamma v)}{64\Gamma^2 v^2}.$$  

(62)

Note that when the frequency shifts are very large, $v \to \infty$, we find using Eq. (61), $\Omega_{\text{max}} \to \infty$. Hence the value of $\Omega_{\text{max}}$ may become very large and then in experiment it is impossible to reach $\Omega_{\text{max}}$ (e.g., $v=1$ GHz). If we impose the condition $\Omega \ll v$ we have

$$Q_{\text{slow}} \approx \frac{\Gamma\Omega^2}{2R(\Gamma^2 + 2\Omega^2)}$$

(63)

for the laser detuning $\omega_L = v$. Hence $Q_{\text{slow}}$ monotonically increases and eventually saturates, similar to the behavior of the average emission rate.

VII. SUMMARY AND DISCUSSION

The $Q$ parameter yields informations not contained in the line shape. The most obvious is the transition from super- (i.e., classical) to sub- (quantum) Poissonian behavior. Such a quantum signature of the photon emission process is not obtained from the line shape. In comparison with the $Q$ parameter of a single atomic transition, the $Q$ parameter investigated here exhibits rich behaviors. These include splitting, both in the sub-Poissonian and in the super-Poissonian regimes, a transition from a fast to a slow modulation limit, and motional narrowing. The most nontrivial behavior is obtained in the intermediate modulation limit when $\Gamma \approx R = \Omega$ where $Q$ attains more than two peaks.

Since $Q$ contains the new information on single molecule experiments, namely, information beyond the line shape, it is important to emphasize that $Q$ attains an extremum for a particular value of the Rabi frequency. In particular, in the sub-Poissonian regime $Q(\Omega)$ has a minimum. Hence we optimize the Rabi frequency in such a way that $|Q|$ is increased, e.g., we obtain $\Omega_{\text{min}}$. In other words there exist an “ideal” choice of the Rabi frequency in single molecule experiments. In the quantum sub-Poissonian regime this optimal Rabi frequency cannot be considered weak, neither strong, hence perturbative approaches to single molecule spectroscopy are not likely to yield it. This is in complete contrast to most theories of line shapes which are based on the assumption of weak external fields, e.g., the Wiener–Khintchine theorem and linear response theory. Single molecule theories should be able to predict the turnover behavior of $Q(\Omega)$ based on different models, since such a behavior is not expected to be limited to the model under investigation. Of course the exact solution presented in this paper is very valuable in this direction, since it predicts precisely the details of this transition for the Kubo–Anderson stochastic process.

It would be interesting to investigate further how general are our results. From line shape theory, we know that in the fast modulation limit, line shapes have Lorentzian shapes under very general conditions. From experiment we know that motional narrowing effect and Lorentzian behavior of lines are widespread. Thus at least in this limit certain general features of line shapes, which are not sensitive to model assumptions, are found. Similarly, we expect that in the fast modulation limit, some of our results are general. Indeed, numerical solutions of several stochastic models show sub-Poissonian behavior. More generally we expect, but have no proof, that motional narrowing behavior of $Q$, and its approach to Mandel’s behavior $Q_M$, is likely to be general. It would be interesting to check if the relation between $Q_{\text{min}}$ and $\Omega_{\text{min}}$, Eqs. (57) and (58), and the width of the line given by $\Gamma_{\text{mod}}$ and $\Gamma$ are valid for other models, both stochastic and Hamiltonian. These simple equations are important since

![Graph](image)

**Fig. 9.** Same as Fig. 8 for the intermediate modulation limit $\Gamma \approx R$. Unlike Figs. 7 and 8, the detuning is on $\omega_L = v$. Parameters are chosen as $\Gamma = 40$ MHz, $\nu = 5\Gamma$, $\Omega = 0 \to 20\Gamma$, and $R = 2\Gamma$. The figure illustrates that the turnover behavior of $Q(\Omega)$ is generic and not limited to the fast modulation limits, Fig. 7, and slow modulation/weak coupling limit, Fig. 8.

![Graph](image)

**Fig. 10.** The crossover behavior of the $Q(\Omega)$ parameter in the slow modulation limit. $Q$ exhibits a super-Poissonian behavior and $Q(\Omega)$ attains a maximum when the Rabi frequency is changed. Thus also for this classical type of behavior an extremum of the fluctuations is found for a particular value of the control parameter $\Omega$. The parameters are $\Gamma = 40$ MHz, $\nu = 5\Gamma$, $R = 500$ Hz and $\omega_L = \omega_S = v$. Using the approximate equations (61) and (62) we obtain the values $Q_{\text{max}} \approx 16$, $\Omega_{\text{max}} \approx 2\Gamma$, denoted by the symbol * in the figure, which is in good agreement with the exact solution (the solid curve).
they yield the optimal Rabi frequency $\Omega_{\min}$ in terms of the width of the line shape, which in turn is easily determined in usual line shape measurement. Another interesting topic not considered in this work, is the time dependence of the $Q$ parameter.\cite{41,42}

In Refs. 25 and 26 a semiclassical framework for the mathematical calculation of $Q$ for single molecule spectroscopy was investigated. The approach yields the $Q$ parameter in terms of a Fourier transform of a three time dipole correlation function. As mentioned in the Introduction, the approach in Refs. 25 and 26 is based on two main approximations: (i) external fields are weak, $\Omega \to 0$, i.e., linear response theory, and (ii) semiclassical approach to photon counting statistics. The second assumption implies that $Q > 0$, and as pointed out in Refs. 15 and 26 such an approach is expected to be valid for slow processes. The approach is useful since most single molecule experiments report on slow fluctuations. The results obtained in this paper reduce to those in Refs. 25 and 26 in the limit of $\Omega \to 0$, and in the slow modulation limit, as they should. The quantum behavior of $Q$ becomes important when $R \sim \Gamma$ or for faster processes. It is left for future work to construct a general quantum linear response theory, based on the equations of motion (9), which would yield both super- and sub-Poissonian statistics.

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