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We derive the moment generating function for photon emissions from a single molecule driven by laser excitation. The frequencies of the fluoresced photons are explicitly considered. Calculations are performed for the case of a two-level dye molecule, showing that measured photon statistics will display a strong and nonintuitive dependence on detector bandwidth. Moreover, it is demonstrated that the antibunching phenomenon, associated with negative values of Mandel’s $Q$ parameter, results from correlations between photons with well separated frequencies.

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In previous work, we [11] and others [6,12] have introduced the generating function formalism for calculation of single-molecule photon counting statistics without spectral resolution. Such broadband photon statistics may be calculated by monitoring the number of times that spontaneous emission occurs as the molecule evolves. Within the Markovian limit for molecular dynamics, spontaneous emission is a simple rate process and these emission events may be treated purely classically, even though the underlying dynamics may involve facets of quantum evolution. Calculation of photon counting moments proceeds via introduction of the generating function for spontaneous emission events $G(s, t) = \langle s^{n(t)} \rangle$ where $n(t)$ is the number of emissions in the interval $[0, t]$ and the factorial moments of this quantity follow immediately by differentiating $G$ with regard to the auxiliary variable $s$ and evaluating at $s = 1$. The equations of motion for $G(s, t)$ (and by extension the factorial moments) involve only minimal complications beyond the usual quantum master equation approach used to solve for density matrix dynamics [11].

In contrast to the above, if the frequency of emitted photons is measured, it becomes impossible to proceed via simple classical arguments. Decay of an electronic excitation into a particular field mode or narrow subset of modes cannot be monitored by simply counting instantaneous spontaneous emission “events”; such a process is fundamentally non-Markovian. However, the definition of the generating function may be generalized to allow for calculation of factorial moments with frequency resolution by explicitly introducing a quantum mechanical description of the radiation field. We take

$$G(\tilde{s}, t) = \left\langle \exp \left[ \sum_{k \neq 0} \ln(s_{k \neq 0}) a_{k \neq 0}^\dagger(t) a_{k \neq 0}(t) \right] \right\rangle$$

$$= \left\langle \mathcal{N} \exp \left[ \sum_{k \neq 0} (s_{k \neq 0} - 1) a_{k \neq 0}^\dagger(t) a_{k \neq 0}(t) \right] \right\rangle .$$  \hspace{1cm} (1)

Here, the averaging operation has its usual meaning $\langle \cdots \rangle = \text{Tr}\{\cdots \rho(0)\}$ involving the initial density matrix.
and a full trace over both the fluorophore and radiation field degrees of freedom. Creation and annihilation operators for photons with wave vector \( \mathbf{k} \) and polarization \( \mathbf{e} \) have been introduced to express \( \exp{i\hat{\mathbf{e}}(t)} \) from the broadband definition as \( \exp[\ln(s)\sum_{k\epsilon}N_{k\epsilon}(t)] \) with \( N_{k\epsilon}(t) = a_k^\dagger(t)a_k(t) \) representing the Heisenberg picture number operator for each mode. The generalization from \( s \) to \( \bar{s} \) has been made to facilitate extraction of spectral information. The second equality, involving the normal ordering operator \( \exp{-\hat{\mathbf{e}}(t)} \), describes the interaction between the applied laser field (assumed monochromatic coupling between the applied laser field and the system within the dipole approximation \( \mathbf{D} = \mu_0(D^+ + D^-) \) is the dipole moment operator for the system consisting of terms that raise (+) and lower (−) the electronic state of the system) and rotating wave approximation (RWA) [10]. \( \hat{H}_I \) describes the interaction between the system and the modes of the quantized electromagnetic field, also within the dipole approximation \( \hat{H}_I = \gamma \sum_{k\epsilon}[-(\mathbf{e} \cdot \mu_0)D^+a_{k\epsilon} + \text{H.c.}] \). Equation (1) provides a theoretical route toward arbitrary photon counting moments. For simplicity and to make connection with possible experiments, we specialize to the case that photon detection is insensitive to propagation direction and polarization of the emitted photons and also assume that the detectors have finite resolution, registering the arrival of all photons within a window of width \( \Delta \) around a central frequency \( \omega \). We define a number operator for photons within this window

\[
N_{(\omega, \Delta)} = \sum_{k\epsilon}N_{k\epsilon}.
\]  

Combining the above definition with Eqs. (2) and (6) and proceeding to the continuum limit \( \nu \rightarrow \nu(t) \) leads to the conclusion that

\[
\langle N_{(\omega, \Delta)}^{(m)}(t) \rangle = \left( \mathcal{T}_N \left[ \frac{\Gamma_0}{2\pi} \int_{-\Delta/2}^{\Delta/2} \! d\omega_1 \int_0^t \tilde{D}^+(\nu)\tilde{D}^-(\nu) \right] \right)^m e^{-i\omega_0 t}
\]

where \( \Gamma_0 = \mu_0^2/3\pi\varepsilon_0 c^3 \). Equation (8) applied to the case \( m = 1 \) counts, on average, the number of photons within a given frequency window emitted in time \( t \) by the externally excited molecule. The time derivative of

\[
a_{k\epsilon}(t) = e^{-i\omega_0 t} \left[ a_{k\epsilon}(0) + \frac{\gamma}{\hbar} \int_0^t \langle \mathbf{e} \cdot \mu_0 \rangle \tilde{D}^-(\tau)e^{i\omega_0 \tau} d\tau \right],
\]  

and the conjugate expression for \( a_{k\epsilon}^\dagger(t) \). For later convenience, we have introduced the slowly varying rotating-frame operators \( \mathcal{D}^\pm(t) = D^\pm(t)e^{i\omega_0 t} \) and have set \( \omega_{k\epsilon} = \omega_k - \omega_L \). From this, it is readily seen that \( a_{k\epsilon}(t) \) commutes with \( a_{k\epsilon}(t) \) and similarly for \( a_{k\epsilon}^\dagger(t) \). This fact, along with the assumption that the initial time total (system and radiation field) density matrix is a direct product between the system and the vacuum state for the field [i.e., \( \rho(0) = \sigma_i(0) \otimes [0]/[0] \)], allows us to reformulate Eq. (1) as

\[
G(t, \bar{s}) = \left\{ \mathcal{T}_N \exp\left[ \frac{\gamma^2}{\hbar^2} \sum_{k\epsilon} (s_{k\epsilon} - 1) \right] \int_0^t \int_0^t \langle \mathbf{e} \cdot \mu_0 \rangle^2 \mathcal{D}^+(\nu) \times \mathcal{D}^-(\nu)e^{-i\omega_0 (\mu-\nu) d\mu d\nu} \right\}.
\]  

The operator \( \mathcal{T}_N \) acts on all operators to the right of it by first arranging all ‘‘+’’ operators to the left of all ‘‘−’’ operators and subsequently placing all ‘‘−’’ operators in standard time order (latest times at the left) and all ‘‘+’’ operators in reversed time order (latest times at the right). The advantage of Eq. (6) over either expression in Eq. (1) is that the generating function is now defined solely in terms of the evolution of the system, which allows us to pursue actual calculations as detailed below.

The Hamiltonian equations of motion for the creation and annihilation operators evolving with dynamics dictated by Eq. (3) may be formally integrated to yield

\[
\frac{\partial^{n+m}G(s, t)}{\partial s_k \partial s_{k'}^{n+m}} = \langle \mathcal{N}^{(n)}(t)\mathcal{N}^{(m)}_{k'}(t) \rangle
\]

\[
= \langle [a_{k\epsilon}^\dagger(a_{k\epsilon}^\dagger)^m(a_{k\epsilon}^\dagger)^m(a_{k\epsilon})^n](t) \rangle,
\]  

with the expected generalization applying to modes involving more than two modes. The above introduces the notation \( \mathcal{N}^{(m)} \equiv N(N - 1) \ldots (N - m + 1) \).
this quantity evaluated in the $t \to \infty$ limit reproduces the usual expression [10,15] for the spectrum of fluorescent radiation. Also, in the limit that $\Delta \to \infty$, Eq. (8) reduces to Mandel’s expression [16] for the factorial moments of photon emission as detected in broadband measurements (i.e., no frequency resolution).

The $\mathcal{T}_N^*$ operator in Eq. (8) ensures that all correlation functions appearing in $\langle N_{\omega,\Delta}^{(m)}(t) \rangle$ are of the form

$$
\langle \hat{D}^+(u_1)\hat{D}^+(u_2)\ldots\hat{D}^+(u_m)\hat{D}^-(v_m)\hat{D}^-(v_{m-1})\ldots\hat{D}^-(v_1) \rangle
$$

(9)

with $u_m \geq u_{m-1} \geq \ldots \geq u_1$ and $v_m \geq v_{m-1} \geq \ldots \geq v_1$. Correlation functions with such time ordering may be calculated within in the Markov limit for system dynamics via an extension of the quantum regression theorem [17]. It follows that the explicit calculation of moments in Eq. (8) is straightforward in principle, involving only diagonalization of the rotating-frame evolution operator for system dynamics and elementary integrals over time and frequency. The procedure will be specified in detail elsewhere.

For concreteness, we present predictions for the low temperature spectroscopy of a single two-level dye molecule. We take $H_s = (\hbar\omega_0/2)[|e\rangle\langle e| - |g\rangle\langle g|]$ and $\hat{D} = |e\rangle\langle g| (\hat{D}^* = |g\rangle\langle e|)$ with $e$ and $g$ designating excited and ground states. Traditionally, the spontaneous emission rate $\Gamma_0$ and the Rabi frequency $\Omega = E_L / \mu_0 / \hbar$ [10] are specified in lieu of $\mu_0$ and $E_L$ and we follow this convention here. We take $\Gamma_0/2\pi = 40$ MHz in all that follows to model the organic dye terpy in a hexadecane Shpol’skii matrix at 1.7 K, a prototypical two-level SMS system [18]. The following calculations assume $\Delta$ values ranging from 0.2 to 200 MHz. Resolution down to 2 MHz is possible using a Fabry-Perot interferometer [19]. Theoretically, it should be possible to measure the reported quantities; however, such measurements have not previously been reported. (Emission line shapes measured via ensemble experiments [19] are in agreement with our results and previous theories [10,15].)

A traditional measure of broadband photon statistics is Mandel’s $Q$ parameter [16], which is defined as the ratio of the second factorial cumulant of $N_{\omega,\Delta}(t) = N(t)$ to the first factorial cumulant (i.e., the average) of $N(t)$, $\mathcal{Q}(t) \equiv [\langle \Delta^2(t) \rangle - \langle \Delta(t) \rangle^2 - \langle \Delta(t) \rangle]/\langle \Delta(t) \rangle$. We introduce a generalization of this quantity appropriate to photon counting within a finite size frequency window

$$
\mathcal{Q}_\Delta(\omega, t) = \frac{\langle N_{\omega,\Delta}^{(2)}(t) \rangle - \langle N_{\omega,\Delta}(t) \rangle^2}{\langle N_{\omega,\Delta}(t) \rangle},
$$

(10)

and $\mathcal{Q}_\infty(\omega, t) = Q(t)$. Figure 1 plots both the emission line shape (with finite resolution) $I(\omega - \omega_0) = \lim_{r \to \infty} \frac{\delta}{\delta \omega} \langle N_{\omega,\Delta}(t) \rangle$ and $\mathcal{Q}_\Delta(\omega, \infty)$ for resonant excitation conditions ($\omega_i = \omega_0$) and $\Delta = \Gamma_0/400\pi = 0.2$ MHz. Two different values of the Rabi frequency are considered: $\Omega = \Gamma_0/\sqrt{2}$ and $\Omega = 5\Gamma_0/\sqrt{2}$. The effect of frequency binning is barely discernible in the line shape when $\Delta$ is chosen so small. Our results are essentially identical to the classical emission spectrum of Mollow [15], excepting the delta function “coherent” [10,15] contribution at $\omega = \omega_L$, which adopts a finite height after frequency binning. Plots for $\mathcal{Q}_\Delta(\omega, \infty)$ have not been reported previously, and at first sight our results appear surprising. The values selected for $\Omega$ in the chosen examples both yield sizable negative values for the traditional broadband $Q$ parameter ($-3/4$ and $-0.11$ for $\Omega = \Gamma_0/\sqrt{2}$ and $\Omega = 5\Gamma_0/\sqrt{2}$, respectively); however, $\mathcal{Q}_\Delta(\omega, \infty)$ is seen to be positive over the entire frequency axis. The implication is that the antibunching phenomenon associated with $\mathcal{Q} < 0$ is due to correlations between photons of different frequencies. To make this point more explicitly, we plot $\mathcal{Q}_\Delta(\omega, \omega)$ for different choices of $\Delta$ in Fig. 2. $\mathcal{Q}_\Delta(\omega, \infty)$ is seen to become negative over portions of the frequency axis as $\Delta$ approaches the width of the peaks in the spectrum. Related behavior has been predicted for the intensity correlation function $(g_2)$ of photons originating from a single well-resolved sideband in the Mollow triplet [8–10]. Interestingly, narrow band bunching has previously been attributed to properties of the detector [9], but we find the same effect in our observables that focus solely on photon emission.

Equation (8) is easily generalized to calculate correlations between photons at different frequencies. We define a normalized photon covariance function as

$$
\mathcal{C}_\Delta(\omega_i, \omega_j, t) = \frac{\langle N_{(\omega_i,\omega_j)}(t) \rangle \langle N_{(\omega_i,\omega_j)}(t) \rangle - \langle N_{(\omega_i,\Delta)}(t) \rangle \langle N_{(\omega_j,\Delta)}(t) \rangle}{\sqrt{\langle N_{(\omega_i,\Delta)}(t) \rangle \langle N_{(\omega_j,\Delta)}(t) \rangle}}
$$

(11)

and $\mathcal{C}_\infty(\omega_i, \omega_j, t) = \mathcal{C}(\omega_i, \omega_j, t)$. The limit $t \to \infty$ of this correlation function is plotted in Fig. 3, where $\omega_{i(j)}$ have been chosen to follow $\omega_i = \omega_0 + r\Delta$ and $r$ is any integer. When $\omega_i = \omega_j$, $\mathcal{C}_\Delta(\omega_i, \omega_j, t) = \mathcal{Q}_\Delta(\omega_i, t)$. Otherwise, $\mathcal{C}_\Delta(\omega_i, \omega_j, t)$
and the same cases as in Fig. 1. The bar graph format is used to emphasize the size and location of the frequency bins, but is absent at the finest discretization for clarity.

simply represents the covariance in photon number, normalized so as to give a finite result in the long time limit. Figure 3 demonstrates that although \( Q_\Delta(\omega, t = \infty) \) is 0, the total \( Q \) parameter is dominated by negative contributions from photons that are well separated in frequency; broadband measurement of \( Q \) contains important contributions from correlations spanning the entire spectrally active region of the transition. The positive intersideband peaks in Fig. 3 reflect the correlated emission of photons from opposite sidebands. This is in qualitative agreement with the intersideband bunching expected for a two-level system excited far from resonance [8]. The phenomenon is attributable to the necessary paring of photons from the two sidebands in order to maintain total energy conservation as photons of energy \( \hbar \omega_L \) are absorbed by the molecule.

Our treatment of photon emission statistics is general and relies on no approximations beyond the RWA and Markov assumption for system dynamics. It is valid for arbitrary field strengths and does not assume particular physical regimes for the molecular system. Moreover, the present approach provides photon correlations between all possible frequency pairs, which enables calculation for any possible detector bandwidth and a quantitative demonstration of how seemingly inconsistent broadband versus narrow band statistics can arise from the same physical phenomena. This framework should prove valuable in the interpretation of future SMS experiments and in understanding the molecular dynamics that such measurements probe. Several multistate dye models are discussed in Ref. [7] and will be treated in a future study.

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FIG. 2 (color online). \( Q_\Delta(\omega, t = \infty) \) for different values of \( \Delta \) and the same cases as in Fig. 1. The bar graph format is used to emphasize the size and location of the frequency bins, but is absent at the finest discretization for clarity.

FIG. 3 (color online). Contour plot of the normalized factorial covariance function [see Eq. (11)]. We consider the \( \Omega = 5\Gamma/\sqrt{2} \) case of Figs. 1 and 2 and have set \( \Delta = 2 \) MHz.

[14] We assume the electronic splitting far exceeds any nuclear energy scales in the system, and have replaced \( \omega_k \) with the standard expression for \( y \) with \( \omega_0 \).