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Photon Statistics of Resonance Fluorescence in the Limit of Separated Spectral Lines

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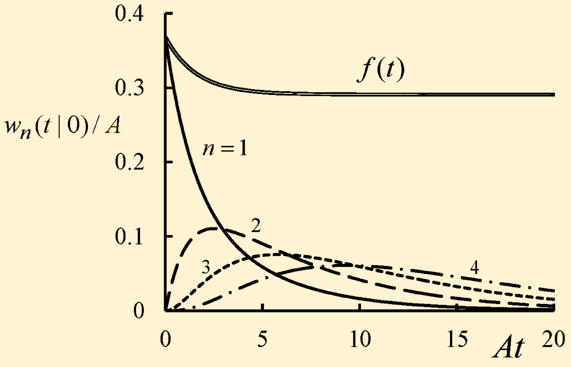
ABSTRACT: We have studied the statistics of fluorescent photons emitted by a two-state atom in a laser beam in the limit where either the detuning or the Rabi frequency is large. For this case, the spectrum of resonance fluorescence has three separated lines. We have obtained closed form expressions for the conditional probability density for the emission of the nth photon and for the probability for emission of n photons in a time interval $[0,T]$. Our solutions are complementary to the known solutions for the case of perfect resonance.



1. INTRODUCTION

When laser light impinges on a sample, depending upon the excitation wavelength, different types of spontaneous emissions may appear. If the excitation falls in a region of electronic absorption, some emission features appear to originate from those excited-state molecular levels resonant with the incident excitation, and they correspond to the energy-level spacings between the excited and ground electronic states. Their bandwidths correspond to electronic relaxation parameters, accounting for mechanisms in the fluorescence event, a feature, together with Raman events, of the resonant secondary radiation spectrum. Resonance fluorescence events are crucial to understand laser-excited resonance emission from electronically excited states and to obtain structural and dynamical information on chemical systems. Indeed, the phase coherence of two radiation-coupled levels can be destroyed by mechanisms such as lifetime effects (typical of the system under investigation) or environmental effects (typically of the solvent). The relaxation rates of these events are directly related to the observed vibrational or electronic line widths in the emission intensity, in which the component due to resonance fluorescence alone cannot be easily separated out experimentally.

For instance, as the pioneering work of Ziegler's group has demonstrated,[1−3] the absorption spectra of methyl-iodide vapor have quite different lineshapes, depending on whether CH_3I is taken pure or with a background gas as solvent (such as methane at pressures above 10 atm). Those differences have unequivocally been attributed to the resonance fluorescence mechanism. Or, as another example, again from Ziegler's work, the ArF excimer-laser excitation spectrum of molecular oxygen shows a structure that is more complex than the coherent, narrow-band Raman spectrum, with the former showing a resonance fluorescence contribution, which is missing in the latter.

It is therefore of utmost importance to be able to quantify the resonance fluorescence contribution, whose importance increases with the increase of stochastic interactions as in the above examples. It is in recognition of this importance that we have considered the problem of studying the statistics of fluorescent photons emitted by a two-level transition in a laser beam.

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2. STATEMENT OF THE PROBLEM

A two-state atom in a laser beam undergoes stimulated excitation and decay, which are accompanied by the absorption and emission of a photon from the laser mode, respectively. In addition, when the atom is in the excited state, it spontaneously decays to the ground state, and in this process a fluorescent photon is emitted. This fluorescence is emitted in all directions as electric dipole radiation and is amenable to measurement by a detector in the far field. The observation of photons is a random event process on the time axis, and for such a process all statistical information is contained in the k-fold intensity correlation functions, defined as[4]

$$\begin{aligned} I_k(t_1, ..., t_k)\mathrm{d}t_1...\mathrm{d}t_k &= \text{probability for a photon detection in} \\ &\quad [t_1, t_1 + \mathrm{d}t_1] \text{ and...and a photon detection in} \\ &\quad [t_k, t_k + \mathrm{d}t_k], \text{ irrespective of detections at other} \\ &\quad \text{times, and with } t_1 < ... < t_k \end{aligned} \tag{1}$$

The function $I_1(t)$ is the intensity of the process. Photons in resonance fluorescence from a single atom are obviously correlated since the emission of a photon in spontaneous decay leaves the atom in the ground state immediately after the emission. This will affect the probability for the emission of the subsequent photon. The atom needs to be in the excited state before the next photon can be emitted, and therefore, the probability for emission of a second photon immediately after the first one is zero. This phenomenon is called antibunching and has been experimentally observed.[5−7]

The intensity correlation functions determine all other temporal statistical properties of the photon counting process. Most notably, the probability for the detection of exactly n photons in the time interval $[t_a,t_b]$ can be obtained. This statistical function, indicated by $P_n(t_a,t_b)$ has been studied extensively for resonance fluorescence.[8−10] Also of interest are the conditional probability densities $w_n(t_a,t|t_a)$, which are defined as $w_n(t_a,t|t_a)\mathrm{d}t$ = probability that the nth photon is detected in $[t,t + \mathrm{d}t]$, after a photon detection in $[t_a - \mathrm{d}t_a,t_a]$. In other words, if we indicate by τ_n the time at which the nth photon is detected, after a detection in $[t_a - \mathrm{d}t_a,t_a]$, then the t dependence of $w_n(t_a,t|t_a)$ is the probability density function for τ_n. This function has also been considered by several authors for resonance fluorescence.[11,12]

The probabilities $P_n(t_a,t_b)$ must satisfy the sum rule

$$\sum_{n=0}^{\infty} P_n(t_a, t_b) = 1 \tag{2}$$

since the left-hand side equals the probability to find any number of photons in $[t_a,t_b]$. The sum rule for the conditional probability densities is[10]

$$\sum_{n=1}^{\infty} w_n(t_a, t|t_a) = \frac{I_2(t_a, t)}{I_1(t_a)} \tag{3}$$

which holds for any random event process.

Correlations between fluorescent photons and the associated statistics have been studied for decades by numerous authors, both theoretically and experimentally. Although the formalism is well-understood, it appears to be difficult to obtain explicit results for the various statistical functions. The probabilities and the conditional probability densities have been found in closed form for the case of perfect resonance between the laser frequency and the atomic transition. In this article we shall consider the case of high laser power and/or large detuning from resonance and obtain closed form results.

3. RESONANCE FLUORESCENCE

When photons are detected from electromagnetic radiation with a photomultiplier tube, the response of the detector is determined by the electric field $E(t)$ at the location of the detector. The photon intensity correlation functions are[13,14]

$$I_k(t_1, ..., t_k) = \zeta^k \langle E(t_1)^{(-)}...E(t_k)^{(-)}E(t_k)^{(+)}...E(t_1)^{(+)}\rangle \tag{4}$$

with $E(t)^{(+)}$ and $E(t)^{(-)}$ the positive and negative frequency parts of the electric field, respectively, and ζ an overall constant. The time dependence of the electric field represents the Heisenberg picture of this operator, and the notation $\langle ...\rangle$ indicates the quantum average.

For a two-state atom, with excited state $|e\rangle$ and ground state $|g\rangle$, the positive frequency part of $E(t)$ is proportional to the lowering operator $|g\rangle\langle e|$ in the Heisenberg picture, and $E(t)^{(-)}$ is the Hermitian conjugate of $E(t)^{(+)}$. Working out eq 4 then yields[15]

$$I_k(t_1, ..., t_k) = (\alpha A)^k f(t_k - t_{k-1})...f(t_2 - t_1)n_\mathrm{e} \tag{5}$$

for $k = 2, 3$, etc. It is assumed that the atom is in the steady state, and n_e is the population of $|e\rangle$ in the steady state. The function $f(t)$ is equal to the population of the excited state at time t, under the condition that the atom is in the ground state at time zero. The constant A is the Einstein coefficient for spontaneous decay, and α has the significance of the probability that an emitted photon is detected. The intensity of the process is

$$I_1 = \alpha A n_\mathrm{e} \tag{6}$$

which is independent of time in the steady state. We clearly have $f(0) = 0$, which reflects the antibunching of subsequent photons, and $f(\infty) = n_\mathrm{e}$.

In the steady state, the probabilities $P_n(t_a,t_b)$ only depend on the counting time $T = t_b - t_a$, and not on the two times separately. We shall therefore write $P_n(T)$ for the probabilities. Similarly, the conditional probability density functions $w_n(t_a,t|t_a)$ are independent of t_a, and we write $w_n(t|0)$. It follows from eq 5 that all statistical properties of the fluorescent photons are contained in the function $f(t)$, and therefore, $P_n(T)$ and $w_n(t|0)$ are determined by $f(t)$. In terms of the Laplace transform of $f(t)$

$$\tilde{f}(s) = \int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st} f(t) \tag{7}$$

the Laplace transform of $w_n(t|0)$ is[16]

$$\tilde{w}_n(s|0) = \left(\frac{\alpha A\tilde{f}(s)}{1 + \alpha A\tilde{f}(s)}\right)^n \tag{8}$$

Similarly, the Laplace transform (in T) of $P_n(T)$ is

$$\tilde{P}_0(s) = \frac{1}{s} - \frac{I_1}{s^2}\frac{1}{1 + \alpha A\tilde{f}(s)} \tag{9}$$

$$\tilde{P}_n(s) = \frac{I_1}{s^2}\frac{[\alpha A\tilde{f}(s)]^{n-1}}{[1 + \alpha A\tilde{f}(s)]^{n+1}} \qquad n = 1, 2, ... \tag{10}$$

It is verified easily that

$$\sum_{n=0}^{\infty} \tilde{P}_n(s) = \frac{1}{s} \tag{11}$$

which is eq 2 in the Laplace domain. Sum rule 3 becomes

$$\sum_{n=1}^{\infty} w_n(t|0) = \alpha A f(t) \tag{12}$$

for resonance fluorescence, and this can be checked with eq 8.

The functions $P_n(T)$ and $w_n(t|0)$ are determined by $f(t)$, which depends on the details of the atom−laser interaction. In addition, there is a dependence on the parameter α. Experimentally, this is a small number, say 10^{-3}, because only a small fraction of the emitted photons is detected. Interestingly, the statistical functions for arbitrary α (photon detection) can be expressed in terms of the same functions for $\alpha = 1$ (photon emission). If we temporarily set $P_n(T;\alpha)$ for the probabilities for photon detection, then we have[7]

$$P_n(T;\,\alpha) = \sum_{m=n}^{\infty} \binom{m}{n} \alpha^n (1-\alpha)^{m-n} P_m(T;\,1) \tag{13}$$

Similarly,

$$w_n(t|0;\,\alpha) = \sum_{m=n}^{\infty} \binom{m-1}{n-1} \alpha^n (1-\alpha)^{m-n} w_m(t|0;\,1) \tag{14}$$

Therefore, we only need to consider the statistics of photon emission ($\alpha = 1$), which is a great simplification. From here on, we only consider $\alpha = 1$, and we proceed to find an expression for the function $\tilde{f}(s)$.

Let $\hbar\omega_0$ be the energy separation between the ground state and the excited state, and let $\boldsymbol{\mu}$ be the electric dipole operator of the atom. The transition dipole moment matrix element is $\mathbf{D} = \langle g|\boldsymbol{\mu}|e\rangle$. The Einstein A coefficient is

$$A = \frac{{\omega_0}^3}{3\pi\varepsilon_0 \hbar c^3} \mathbf{D}^* \cdot \mathbf{D} \tag{15}$$

The electric field of the laser beam at the position of the atom is written as $\mathbf{E}(t) = E_0 \operatorname{Re}[\boldsymbol{\varepsilon}_L \exp(-i\omega_L t]$. The parameter for the interaction between the atom and the laser field is

$$\Omega = \frac{E_0}{\hbar} \mathbf{D}^* \cdot \boldsymbol{\varepsilon}_L \tag{16}$$

and the detuning from resonance is

$$\Delta = \omega_L - \omega_0 \tag{17}$$

The function $f(t)$ is determined by the equation of motion for the atom in the laser beam. We find[17]

$$\tilde{f}(s) = \frac{{\Omega_0}^2}{2s} \frac{\frac{1}{2}A + s}{(A+s)\left[\left(\frac{1}{2}A + s\right)^2 + \Delta^2\right] + \left(\frac{1}{2}A + s\right){\Omega_0}^2} \tag{18}$$

where $\Omega_o = |\Omega|$ is the Rabi frequency. The steady-state population is then found to be

$$n_e = f(\infty) = \lim_{s \to 0} s\tilde{f}(s) = \frac{{\Omega_0}^2}{A^2 + 4\Delta^2 + 2{\Omega_0}^2} \tag{19}$$

The function $f(t)$ is the Laplace inverse of the right-hand side of eq 18. We see that this would require factoring a third-degree polynomial. For $\Delta = 0$, the numerator in eq 18 simplifies to a second-degree polynomial, and the inverse $f(t)$ can be found easily.[18]

4. LIMIT OF SEPARATED LINES

For the important case of resonance, $\Delta = 0$, the functions $P_n(T)$ and $w_n(t|0)$ can be obtained in closed form.[10,12] Here we shall consider a different case of practical interest. The atom in the laser field can be considered as a single system, known as the dressed atom. In terms of the parameter

$$\Omega' = \operatorname{sgn}(\Delta)\sqrt{\Delta^2 + {\Omega_0}^2} \tag{20}$$

the Bohr frequencies of the system are $\omega_L - \Omega'$, ω_L, and $\omega_L + \Omega'$. Spontaneous emission results in transitions between the eigenstates of the dressed atom and gives spectral lines at these three frequencies.[19] This three-line spectrum of resonance fluorescence is known as the Mollow triplet.[20] The widths of the lines are a result of the finite lifetime of the excited state and are of the order of the Einstein A coefficient. When $|\Omega'|$ is much larger than A, the lines are well separated. This happens for high laser power (Ω_o large compared to A) and/or large detuning from resonance ($|\Delta|$ large compared to A). The condition $|\Omega'| \gg A$ justifies the so-called secular approximation in which couplings between eigenstates of the dressed atom (in Liouville space) with different frequencies are neglected.

The secular approximation greatly simplifies the computation of the spectrum of resonance fluorescence,[21] and along similar lines the function $f(t)$ can be obtained. It appears that $f(t)$ contains a term that oscillates with angular frequency $|\Omega'|$. Such fast oscillations can not be resolved in photon counting, and therefore this term should be dropped (it averages to zero upon integration). We thus find

$$f(t) = n_e\left[1 + \left(\frac{\Delta}{\Omega'}\right)^2 e^{-\beta A t}\right] \tag{21}$$

with

$$n_e = \frac{{\Omega_0}^2}{4\Delta^2 + 2{\Omega_0}^2} \tag{22}$$

the population of the excited state in the secular limit, and the parameter β is defined as

$$\beta = \frac{1}{2}\left[1 + \left(\frac{\Delta}{\Omega'}\right)^2\right] \tag{23}$$

We see that $1/2 \le \beta \le 1$. The function $f(t)$ decays exponentially, with decay time $1/(\beta A)$. The lifetime of the excited state, due to spontaneous emission, is $1/A$, and therefore the function $f(t)$ decays slower than the excited state by a factor of at most 2. Figure 1 shows the exact function $f(t)$ and its secular approximation with the fast oscillations dropped.

For the exact solution we have $f(0) = 0$, which expresses the antibunching of subsequent photons. In the secular limit this remains valid, but when we drop the fast oscillating term we have $f(0) = 2\beta n_e \ge f(\infty)$. Therefore, when the fast oscillations are not resolved, it appears as if the photons are bunched for short time delays. We see indeed from Figure 1 that $f(0) = 0$ for the exact curve, but for the approximation of $f(t)$ we have $f(0) \ge f(\infty)$. Explicitly, we have

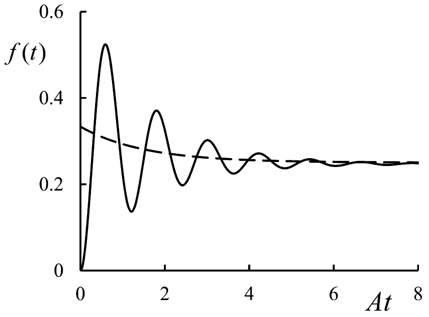

Figure 1. Solid curve is the exact $f(t)$ for $\Delta = 3A$ and $\Omega_o = 4.25A$, so $\Omega' = 5.2A$. Dashed curve is the secular approximation with the fast oscillations dropped.

$$f(0) = \frac{1}{2}\left(\frac{\Omega_0}{\Omega'}\right)^2 \tag{24}$$

The Laplace transform of eq 21 is

$$\tilde{f}(s) = n_e\beta\frac{2s + A}{s(s + \beta A)} \tag{25}$$

This can also be written as

$$\tilde{f}(s) = \frac{{\Omega_0}^2}{2s}\frac{\frac{1}{2}A + s}{(A + s)\Delta^2 + \left(\frac{1}{2}A + s\right){\Omega_0}^2} \tag{26}$$

In this form it has a striking resemblance with the exact expression in eq 18.

5. CONDITIONAL PROBABILITY DENSITY FUNCTIONS AND PROBABILITIES

With use of expression 26 for $\tilde{f}(s)$, the Laplace transforms of the conditional probability densities become (with $\alpha = 1$)

$$\tilde{w}_n(s|0) = \left(\frac{1}{2}A\right)^n\left(\frac{\Omega_0}{\Omega'}\right)^{2n}\left(\frac{s + \frac{1}{2}A}{\left(s + \frac{1}{2}A\right)^2 - (\gamma A)^2}\right)^n$$

$$n = 1, 2, ... \tag{27}$$

and here we have set

$$\gamma = \frac{1}{2}\frac{\Delta}{\Omega'} \tag{28}$$

This parameter lies in the range $0 \leq \gamma \leq 1/2$. The solution for $t = 0$ can be obtained as

$$w_n(0|0) = \lim_{s\to\infty} s\tilde{w}_n(s|0) = \frac{1}{2}A\left(\frac{\Omega_0}{\Omega'}\right)^2\delta_{n1} \tag{29}$$

and this is with eq 24

$$w_n(0|0) = Af(0)\delta_{n1} \tag{30}$$

In order to obtain the Laplace inverse of the right-hand side of eq 27, we first use the attenuation theorem:

$$w_n(t|0) = \left(\frac{1}{2}A\right)^n\left(\frac{\Omega_0}{\Omega'}\right)^{2n} e^{-At/2}\mathcal{L}^{-1}\left\{\frac{s^n}{[s^2 - (\gamma A)^2]^n}\right\} \tag{31}$$

The remaining Laplace inverse can be computed with the Bromwich inversion integral. We find

$$w_n(t|0) = A\left(\frac{\Omega_0}{2\Omega'}\right)^{2n} e^{-At/2}(At)^{n-1} \sum_{k=0}^{n-1}\frac{1}{(n-1-k)!}\frac{1}{(\gamma At)^k} [e^{\gamma At} + (-1)^k e^{-\gamma At}]C_{n,k} \tag{32}$$

The combinatorial functions $C_{n,k}$ are defined in the next section.

It is shown in Appendix A that the result from eq 32 can also be written as

$$w_n(t|0) = 2A\left(\frac{\Omega_0}{2\Omega'}\right)^{2n} e^{-At/2}(At)^{n-1} \sum_{k=0}^{n-1}\frac{1}{(n-1-k)!}C_{n,k}\zeta_k(\gamma At) \tag{33}$$

with the functions $\zeta_k(x)$ defined by eq A9. The first few then become

$$w_1(t|0) = 2A\left(\frac{\Omega_0}{2\Omega'}\right)^2 e^{-At/2}\cosh(x) \tag{34}$$

$$w_2(t|0) = 2A\left(\frac{\Omega_0}{2\Omega'}\right)^4 e^{-At/2}At\left[\cosh(x) + \frac{1}{x}\sinh(x)\right] \tag{35}$$

$$w_3(t|0) = A\left(\frac{\Omega_0}{2\Omega'}\right)^6 e^{-At/2}(At)^2\left[\cosh(x) + \frac{3}{x}\sinh(x)\right] \tag{36}$$

with $x = \gamma At$. Figure 2 shows $w_n(t|0)/A$ for $\Delta = 3A$, $\Omega_0 = 5A$, and $n = 1, 2, 3$, and 4. According to the sum rule 12, the sum over all n should be $f(t)$, eq 21, which is also shown in the figure. We see from the figure that for large n the curves are very flat.

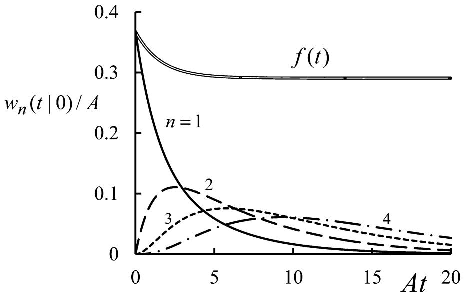

Figure 2. Shown are the conditional probability densities $w_n(t|0)/A$ for $\Delta = 3A$, $\Omega_0 = 5A$, and $n = 1, 2, 3$ and 4, as a function of At. The sum over all n equals $f(t)$. We see from the figure that for moderate t there must be contributions from a large number of functions $w_n(t|0)/A$ in order to reach the sum $f(t)$.

The probability of finding no photons in the counting interval $[0,T]$ is the Laplace inverse of eq 9. We find

$$P_0(T) = e^{-At/2}\left[\cosh(y) + \frac{2\gamma}{\beta}\sinh(y)\right] \tag{37}$$

with $y = \gamma AT$. The probability for the emission of one photon follows from eq 10 with $n = 1$:

$$P_1(T) = \frac{n_e}{2\gamma} e^{-At/2}[(1 + 4y\gamma - 4\gamma^2)\sinh(y) + y(1 + 4\gamma^2)\cosh(y)] \qquad (38)$$

The expression for arbitrary n is rather lengthy and is given in Appendix B. Figure 3 shows $P_n(T)$ for $\Delta = 3A$, $\Omega_0 = 5A$, and $n = 0$, 1, and 2.

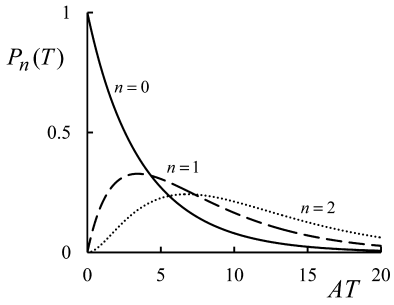

Figure 3. Shown are the probabilities $P_n(T)$ for $\Delta = 3A$, $\Omega_0 = 5A$, and $n = 0$, 1, and 2, as a function of AT.

6. COEFFICIENTS $C_{n,k}$

The coefficients $C_{n,k}$ are defined as

$$C_{n,k} = n \sum_{l=0}^{\min(n,k)} \frac{(n+k-l-1)!}{l!(n-l)!(k-l)!}\left(-\frac{1}{2}\right)^{k-l}$$

$$n = 1, 2, ..., \quad k = 0, 1, ... \qquad (39)$$

and

$$C_{0,k} = \delta_{k0} \quad k = 0, 1, ... \qquad (40)$$

Let us consider some of the properties of these coefficients. The generating function in the second index is found to be

$$\sum_{k=0}^{\infty} C_{n,k} y^k = \left(\frac{1+y}{1+y/2}\right)^n \quad n = 0, 1, ..., \ |y| < 2 \qquad (41)$$

Differentiating with respect to y leads to a three-term recursion relationship in the index k for fixed n:

$$2(k+1)C_{n,k+1} + (3k - n)C_{n,k} + (k-1)C_{n,k-1} = 0$$

$$n = 0, 1, ..., \quad k = 1, 2, ... \qquad (42)$$

The initial values for the recursion can be found from eqs 39 and 40. We have

$$C_{n,0} = 1 \qquad (43)$$

$$C_{n,1} = \frac{1}{2}n \qquad (44)$$

Many other relationships for these coefficients can be found. For example, consider $w_n(t|0)$ as given by eq 32, and set $t = 0$. Only the $k = n - 1$ term contributes to the sum, and we find

$$w_n(0|0) = A\left(\frac{\Omega_0}{2\Omega'}\right)^{2n} \frac{1}{\gamma^{n-1}}(1 - (-1)^n)C_{n,n-1}$$

$$n = 1, 2, ... \qquad (45)$$

For $n = 1$ this gives $w_1(0|0) = A(\Omega_0/\Omega')^2/2$, and this equals $Af(0)$, in agreement with eq 30. For $n > 1$, the right-hand side of eq 45 should vanish. For even n it does, but for odd n the only possibility is that the coefficient $C_{n,n-1}$ is zero. So we obtain

$$C_{n,n-1} = 0 \quad n = 3, 5, 7, ... \qquad (46)$$

Equations A6 and A7 in Appendix A give sum rules for the $C_{n,k}$ coefficients.

The coefficients for $n = 1$ follow eq 39, and we find

$$C_{1,0} = 1 \qquad (47)$$

$$C_{1,k} = \frac{(-1)^{k-1}}{2^k} \quad k = 1, 2, ... \qquad (48)$$

Table 1 shows the coefficients $C_{n,k}$ for several values of n and k.

Table 1. Several Values of the Coefficients $C_{n,k}$

$n\backslash k$	0	1	2	3	4
0	1	0	0	0	0
1	1	1/2	−1/4	1/8	−1/16
2	1	1	−1/4	0	1/16
3	1	3/2	0	−1/4	3/16
4	1	2	1/2	−1/2	−3/16

7. CONCLUSIONS

A two-state atom in a laser beam emits fluorescent photons. The emissions of photons appear as random events on the time axis. We have studied the probability density for the emission of the nth photon, after an initial emission at time zero. We have also studied the probability for the emission of n photons in a time interval $[0,T]$. The parameters of the system are the detuning Δ between the laser frequency and the atomic transition frequency of the two-state atom, and the Rabi frequency Ω_0, which is proportional to the electric field amplitude of the laser. The third parameter is the Einstein A coefficient, but this parameter is used for frequency and time scales. The detuning and Rabi frequency are given in units of A, and time is scaled as At or AT.

The parameter $|\Omega'|$, defined in eq 20, is assumed to be large. This implies that either $|\Delta|$ or Ω_0 must be large. In this case, the fluorescence spectrum has three separated lines, and the computation of the photon statistics simplifies. The exact solution for $\Delta = 0$ is known in the literature.[10,12] The solution presented here is complementary to this known solution in that it allows for nonzero detuning, including large detuning.

In the solution presented here, the case of resonance, $\Delta = 0$, is included, but the requirement of large $|\Omega'|$ then implies a strong laser field. From eq 21 we then have $f(t) = n_e$, and the intensity correlations from eq 5 become $I_k(t_1,...,t_k) = I_1^{\,k}$, with $I_1 = \alpha A n_e$. This corresponds to a Poisson process, for which the photon emissions and detections are purely random. Hence, a strong laser field washes out any correlations between photons when $\Delta = 0$.

The dynamical information about a radiating system is contained in its relaxation parameters, as mentioned in the introduction. Relaxation processes lead to correlations between emitted fluorescent photons and to non-Poissonian photon statistics. Intrinsic properties of the chemical system are revealed in the structure of the two-photon correlation function, as in Figure 1. Without internal relaxation and/or damping due to the environment, this curve would be flat, indicating an absence of any interaction in the chemical system.

Conversely, the decay time of the system is related to the falloff time of the dashed curve in the figure, and this is a direct measure of the inverse damping constant of the system. However, the decay time of the curve is $1/(\beta A)$, as follows from eq 21, whereas the decay time of the chemical system is $1/A$. It is seen from eq 23 that the decay time of the experimental curve does not only depend on the relaxation time of the system but also on the detuning from resonance and the power of the exciting laser. Similarly, the details of the photon statistical functions in Figures 2 and 3 are determined by the relaxation mechanisms in the chemical system, and as such, information about the chemical system can be obtained from a precise measurement of these functions. For this information to be extracted from experimental data, a detailed understanding of the dependence of these functions on the relaxation parameters is required.

■ APPENDIX A

In deriving result 32 for the conditional probability densities, we used the Laplace inverse

$$\mathcal{L}^{-1}\left\{\frac{s^n}{[s^2-a^2]^n}\right\} = \frac{t^{n-1}}{2^n}\sum_{k=0}^{n-1}\frac{1}{(n-1-k)!}\frac{1}{(at)^k}[e^{at}+(-1)^k e^{-at}]C_{n,k} \quad n=1,2,... \tag{A1}$$

which can be derived with the Bromwich inversion integral. In this form, we have powers of t and exponentials. We now derive several alternative representations, and this will also lead to some interesting relations for the coefficients $C_{n,k}$. To this end, we first represent the exponentials by power series

$$e^{at}+(-1)^k e^{-at} = \sum_{l=0}^{\infty}[1+(-1)^{k+l}]\frac{(at)^l}{l!} \tag{A2}$$

and substitute this in the right-hand side of eq A1. In the sum over k and l we eliminate l in favor of the new variable p by the substitution $p = l - k$, and we split the double sum as

$$\sum_{k=0}^{n-1}\sum_{l=0}^{\infty}(...) = \sum_{p=-n+1}^{0}\sum_{k=-p}^{n-1}(...) + \sum_{p=1}^{\infty}\sum_{k=0}^{n-1}(...) \tag{A3}$$

We have $1 + (-1)^{k+l} = 1 + (-1)^p$. This is zero for odd p and 2 for even p. Then, in the first summation we set $p' = -p$ and drop the prime. This yields

$$\mathcal{L}^{-1}\left\{\frac{s^n}{[s^2-a^2]^n}\right\} = \frac{t^{n-1}}{2^{n-1}}\sum_{p=0,2,...}^{n-1\text{ or }n-2}\frac{1}{(at)^p}\sum_{k=p}^{n-1}\frac{1}{(n-1-k)!(k-p)!}C_{n,k} + \frac{t^{n-1}}{2^{n-1}}\sum_{p=2,4,...}^{\infty}(at)^p\sum_{k=0}^{n-1}\frac{1}{(n-1-k)!(k+p)!}C_{n,k} \tag{A4}$$

We now consider this Laplace transform in the limit where a goes to zero:

$$\lim_{a\to 0}\mathcal{L}^{-1}\left\{\frac{s^n}{[s^2-a^2]^n}\right\} = \mathcal{L}^{-1}\left\{\frac{1}{s^n}\right\} = \frac{t^{n-1}}{(n-1)!} \quad n=1,2,... \tag{A5}$$

On the right-hand side of eq A4, the variable t only appears as powers of t, and therefore, in the limit $a \to 0$, only terms with t^{n-1} should survive. In the second series we have $(at)^p \to 0$, so this entire series vanishes. In the first series we have $(at)^{-p}$, and this seems to diverge, except for $p = 0$. Therefore, all terms with $p \neq 0$ should vanish. This is only possible if the summation over k yields zero, so it should hold that

$$\sum_{k=p}^{n-1}\frac{1}{(n-1-k)!(k-p)!}C_{n,k} = 0 \quad n=3,4,...,\ p=2,4,...,n-1\text{ or }n-2 \tag{A6}$$

The cases $n = 1$ and $n = 2$ are excluded since then we only have $p = 0$. Equation A6 is a sum rule for the coefficients $C_{n,k}$. Then, for $a \to 0$, the only surviving term on the right-hand side is the $p = 0$ term, and this one should give the right-hand side of eq A5. This is only possible if

$$\sum_{k=0}^{n-1}\binom{n-1}{k}C_{n,k} = 2^{n-1} \quad n=1,2,... \tag{A7}$$

and this is the second sum rule for the coefficients $C_{n,k}$. We then find that the right-hand side of eq A4 simplifies to

$$\mathcal{L}^{-1}\left\{\frac{s^n}{[s^2-a^2]^n}\right\} = \frac{t^{n-1}}{2^{n-1}}\sum_{l=0}^{\infty}(at)^{2l}\sum_{k=0}^{n-1}\frac{1}{(n-1-k)!(k+2l)!}C_{n,k} \tag{A8}$$

where we have set $p = 2l$. In this form, the Laplace inverse is a power series in t.

Yet another representation follows by introducing the functions

$$\zeta_k(x) = \sum_{l=0}^{\infty}\frac{x^{2l}}{(k+2l)!} \quad k=0,1,... \tag{A9}$$

This yields

$$\mathcal{L}^{-1}\left\{\frac{s^n}{[s^2-a^2]^n}\right\} = \frac{t^{n-1}}{2^{n-1}}\sum_{k=0}^{n-1}\frac{1}{(n-1-k)!}C_{n,k}\zeta_k(at) \tag{A10}$$

The first few of these functions are

$$\zeta_0(x) = \cosh(x) \tag{A11}$$

$$\zeta_1(x) = \frac{1}{x}\sinh(x) \tag{A12}$$

$$\zeta_2(x) = \frac{1}{x^2}[\cosh(x) - 1] \tag{A13}$$

and functions with higher k can be obtained most easily from the recursion relation

$$\zeta_{k+2}(x) = \frac{1}{x^2}\left[\zeta_k(x) - \frac{1}{k!}\right] \quad k=0,1,... \tag{A14}$$

■ APPENDIX B

The Laplace inverse of the right-hand side of eq 10, with $\alpha = 1$, can be found with the Bromwich integral. The result is

$$
\begin{aligned}
P_n(T) = {} & \frac{1}{4} n_{\mathrm{e}} \left(\frac{\Omega_0}{2\Omega'} \right)^{2n-2} \mathrm{e}^{-At/2} (AT)^n \sum_{k=0}^{n} \frac{1}{y^k} C_{n+1,k} \\
& \times \left(\frac{1}{(n-k)!} [\mathrm{e}^{y} (1 + 2\gamma)^2 + (-1)^k \, \mathrm{e}^{-y} (1 - 2\gamma)^2] \right. \\
& + 4\gamma \sum_{l=1}^{n-k} \frac{1}{(n-k-l)!} \frac{1}{y^l} \{ (-1)^l \, \mathrm{e}^{y} [(l+1)\gamma + 1] \\
& \left. + (-1)^k \, \mathrm{e}^{-y} [(l+1)\gamma - 1] \} \right)
\end{aligned}
\tag{B1}
$$

for $n = 1, 2$, etc. Interestingly, if we set $n = 0$ we find the correct result for $P_0(T)$, provided the empty sum over l is taken to be zero.

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Notes

The authors declare no competing financial interest.

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