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We consider the theory of time-dependent fluctuations in single molecule spectroscopy. In particular, the relation between stationary spectral diffusion processes and photon counting statistics is investigated. Within linear response theory, a general relation between Mandel’s $Q$ parameter and a three time dipole correlation function is obtained. For a prototype spectral diffusion process, an exact solution of $Q$ is found which exhibits rich types of physical behaviors.

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Experimental advances have made it possible to measure the spectral line of a single molecule (SM) embedded in a condensed phase [1]. The statistical properties of the photons emitted from such a SM illuminate the interplay between dynamical processes in the condensed phase, SM dynamics, and light-matter interaction. An important process responsible for the emission pattern of a SM is spectral diffusion; i.e., perturbers such as two level systems or excitations in the environment of the excited SM lead to random changes in the transition frequency of the SM, and in this way the SM comes in and out of resonance with the exciting laser field [2–8]. The fundamental issue addressed in this work is the photon statistics of a single molecule undergoing a spectral diffusion process.

We model these fluctuations in a semiclassical way, using the Bloch equation, in the limit of a weak laser field. The spectral diffusion process is described using a Kubo-Anderson sudden jump approach [9]. The same model leads to a basic understanding of line shape phenomena, i.e., the average number of counts ⟨$n$⟩ per measurement time $T$. Variants of this model have been used in the past to model ensemble measurements, in, e.g., NMR [9] and nonlinear spectroscopy [10]. More recently, this approach was applied to model SM spectroscopy (SMS) in glasses, by Geva and Skinner [11], in [8] to describe static properties of line shapes, and by Plakhotnik [7] to model time-dependent fluctuations of SMS.

In this Letter, we present a general formula for Mandel’s $Q$ parameter [12],

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

where $n$ is the random number of counts. We show how $Q$ is related to the underlying stochastic events and how $Q$ yields new information not contained in the average $\langle n \rangle$. For a simple Kubo-Anderson spectral diffusion process, we find an exact solution for $Q$ which gives insight on the characteristics of SMS fluctuations. If $Q = 0$, the photon count is Poissonian while our semiclassical results show a super-Poissonian behavior $Q > 0$. For short times (e.g., ns), the correlation function between fluorescence photons emitted by a single molecule shows antibunching, a sub-Poissonian nonclassical effect [12–14]. Our approach works well for longer times such that $7T^* \gg 1$, where $T^*$ is the radiative decay rate of the molecule.

The key quantity in the present formulation is a three time correlation function $C_3(\tau_1, \tau_2, \tau_3)$, which is similar to nonlinear response functions investigated in the context of four wave mixing processes [10]. The three time correlation function contains all the microscopic information relevant for the calculation of the line shape fluctuations. It appeared previously in the literature of Plakhotnik [7] in the context of the intensity-time-frequency-correlation technique. In this Letter, important time ordering properties of this function are investigated, and $Q$ is evaluated. The relation between $C_3(\tau_1, \tau_2, \tau_3)$ and line shape fluctuations described by $Q$ generalizes the Wiener-Khintchine theorem, that relates the averaged line shape and the one time dipole correlation function.

Let us briefly mention some of the limitations of our theory. The experimental measurement time $T$ is bounded due to photobleaching. In some cases, this may limit the collection of a sufficient number of counts to build up enough statistics (see counterexamples [15,16], where photostable SMs were used). Besides spectral diffusion, other physical processes may contribute to SMS fluctuations depending on the SM and its environment. These include triplet state dynamics and SM rotational dynamics. The existence of a SM metastable state (lifetime $\geq$ms) leads to a blinking effect, where long periods of brightness with many photon counts are interrupted by periods of darkness of no photon detection ([1] and references therein). Our theory considers the fluctuations in the bright state, which are due to spectral diffusion. Keeping these limitations in mind, we will show below that our theoretical results, in a certain simple limit, describe a SMS experiment [2].

An important issue is the fast and slow modulation limits [9], to be defined later. SMS is often used to detect very slow, time-dependent fluctuations induced by the environment of the single molecule. Fast frequency modulations are much more difficult to detect. For example, we...
find below that $Q \rightarrow 0$ when the frequency modulations become extremely fast. Nevertheless, our work provides insight into the possibility of measuring fast dynamics using SMS.

We assume a simple nondegenerate two state single molecule in an external classical laser field. The first electronic excited state $|e\rangle$ is located at energy $\omega_0$ above the ground state $|g\rangle$. We consider the SM Hamiltonian,

$$H = \frac{\hbar}{2} \omega_0 \sigma_z + \sum_{j=1} \frac{\hbar}{2} \Delta \omega_j(t) \sigma_j - \mathbf{d} \cdot \mathbf{E} \cos(\omega_L t),$$

(2)

where $\sigma_z$ is the Pauli matrix. The second term in $H$ reflects the effect of the time evolution of the environment on the absorption frequency of the SM coupled to $J$ perturbers.

The last term in Eq. (2) describes the interaction between the SM and the laser field (frequency $\omega_L$), while $\mathbf{d} \equiv \mathbf{d}_{eg} \sigma_z$ is the dipole operator with the real matrix element $\mathbf{d}_{eg} = \langle e|\mathbf{d}|g\rangle$.

The molecule is described by $2 \times 2$ density matrix $\rho$ whose elements are $\rho_{ee}$, $\rho_{eg}$, $\rho_{ge}$, and $\rho_{gg}$. Let $u = \text{Re}(\rho_{ge}e^{-i\omega_L t})$, $v = \text{Im}(\rho_{ge}e^{-i\omega_L t})$, and $w = (\rho_{ee} - \rho_{gg})/2$. Using Eq. (2), the stochastic Bloch equations, in the rotating wave approximation, are

$$\dot{u} = \delta_L(t) v - \Gamma u / 2,$n

$$\dot{v} = -\delta_L(t) u - \Omega w - \Gamma v / 2,$n

$$\dot{w} = \Omega v - \Gamma w - \Gamma / 2,$n

where $\Omega = -\mathbf{d}_{eg} \cdot \mathbf{E} / \hbar$ is the Rabi frequency, $\delta_L(t) = \omega_L - \omega_0 - \sum_{j=1} \Delta \omega_j(t)$ is the detuning frequency, and without loss of generality we set $\omega_0 = 0$. SM experiments [17,18] were shown to be compatible with the deterministic two level optical Bloch equation approach, and this gives further justification for our assumptions.

According to semiclassical theory of photon counting statistics [12], the probability of recording $n$ photons in time interval $(0, T)$ is given by

$$p(n, T) = \left( \frac{\langle W \rangle^n}{n!} \exp(-\langle W \rangle) \right),$$

(4)

where $W = \xi \int_0^T I(t) dt$, $I(t)$ is the photon current, and $\xi$ is a suitable constant depending on detection efficiency. The semiclassical approach is valid for a large number of counts, when the stream of incoming absorption photons (i.e., $\Omega v$) is equal to the stream of emitted fluorescence photons (i.e., $\Gamma \rho_{ee}$). We use $W = \xi \Omega \int_0^T v(t) dt$, which is $\xi$ times the work of the driving field per unit energy (defined by $\hbar \omega_L$). Using the Bloch equation (3), it is easy to show that, when $W \gg 1$ (i.e., large photon count), $W \rightarrow \xi \Gamma \int_0^T \rho_{ce}(t) dt$ as expected. Using Eq. (4), the average number of photons counted in time interval $(0, T)$ is $\langle n \rangle = \langle W \rangle$, where $\langle \cdot \cdot \cdot \rangle$ is an average over the stochastic process. Mandel's $Q$ parameter is used to characterize the fluctuations, and it is straightforward to show that

$$Q = \frac{\langle W^2 \rangle - \langle W \rangle^2}{\langle W \rangle}.$$  

(5)

We see that $Q \cong 0$, indicating that photon statistics are super-Poissonian.

We now consider the important limit of weak laser intensity of Eq. (3). We use a straightforward perturbation expansion in the Rabi frequency to find

$$v = \frac{\Omega}{2} \text{Re} \left[ \int_0^T dt \int_0^T dt' \delta_L(t') - \Gamma \frac{(t - t')}{2} \right].$$  

(6)

In standard line shape theories Eq. (6) is averaged. The well-known result gives the Wiener-Khintchine formula for the line shape $\langle I(\omega_L) \rangle = \lim_{T \to \infty} \langle W \rangle / T$, which is valid for stationary processes.

$$\langle I(\omega_L) \rangle = \frac{\xi^2 \Omega^2}{2} \text{Re} \left[ \int_0^T dt \int_0^T dt' e^{-i\omega_L(t-t')} C_1(t) \right].$$  

(7)

Here, $C_1(\tau) = \langle e^{i \sum \Delta \omega_j(t') dt'} \rangle$ is the one time dipole correlation function. Let us now consider the fluctuation,

$$\langle W^2 \rangle = \frac{\xi^2 \Omega^4}{16} \int_0^T \int_0^T \int_0^T \int_0^T dt_1 dt_2 dt_3 dt_4 \times e^{-i\omega_L(t_2-t_1+t_1-t_0)-\Gamma[t_1-t_2]+\Gamma[t_2-t_3]+\Gamma[t_3-t_4]+\Gamma[t_4-t_0]} \times C_3(t_1, t_2, t_3, t_4),$$  

(8)

where the correlation function,

$$C_3(t_1, t_2, t_3, t_4) = \left\langle \exp \left[ i \int_{t_1}^{t_2} \sum_j \Delta \omega_j(t') dt' \right. \right.$$  

$$- i \int_{t_3}^{t_4} \sum_j \Delta \omega_j(t') dt' \right\rangle,$$  

(9)

contains the information on the spectral diffusion process relevant for the calculation of $Q$. To find the correlation function, we must consider the time orderings of $t_1, t_2, t_3, t_4$, for which there are $4! = 24$ options. As we show now, only three of these time ordered correlation functions are needed, provided that the stochastic process is stationary. Let $\{t_1, t_{111}, t_{11}, t_{111}\}$ be the time ordered set of $\{t_1, t_2, t_3, t_4\}$, satisfying $t_1 < t_{11} < t_{111} < t_{11V}$ (e.g., if $t_1 < t_2 < t_3 < t_4$, then $t_1 = t_1, t_2 = t_{11}, t_3 = t_{111}$, and $t_4 = t_{11V}$). Then, due to stationarity, the average in Eq. (9) does not depend on the time elapsed between the start of the observation and $t_1$. In that case, we may write

$$C_3(t_1, t_2, t_3, t_4) = C_3(t_1, t_2, t_3).$$  

(10)

From Eqs. (8)–(10), we learn that a three time (dipole) correlation function describes the stationary line shape fluctuations. Let us consider in some detail the case $t_1 < t_2 < t_3 < t_4$ (i.e., $t_1 = t_1, t_2 = t_{11}, t_3 = t_{111},$ etc.). We define the pulse function $S(t) = -1$ for $t_1 < t < t_{11}$, $S(t) = 0$ for $t_{11} < t < t_{111}$, and $S(t) = 1$ for $t_{111} < t < t_{11V}$; the
We note that pulses 1 and 2 are encountered in the theory of four wave mixing [10].

Equations (5)–(10) give a general prescription for the calculation of \( Q \) for many types of spectral diffusion. Now we investigate basic properties of line shape fluctuations considering a simple process [9]. We assume \( J = 1 \) and \( \Delta \omega(t) = \nu h(t) \) and \( h(t) \) is a random telegraph process \( h(t) = 1 \) or \( h(t) = -1 \). The transition rate from state up (+) to down (−) and vice versa is \( R \).

Using a method of Suárez and Silbey [19], developed in the context of photon echo experiments, we now analyze the properties of the three time correlation function. Define the weights \( P_{ij}^k(t) = \langle \exp[-is \int_0^t \Delta \omega(t') dt'] \rangle_{ij} \) where the initial (final) state of the stochastic process \( \Delta \omega = i (f) \) and \( s = 0 \) or \( +1 \) or \( -1 \) [20]. For example, \( P_{ij}^{k+1}(t) \) is the value of \( \langle \exp[i \int_0^t \Delta \omega(t') dt'] \rangle \) for a path restricted to have \( \Delta \omega(0) = \nu \) and \( \Delta \omega(t) = \nu \). Using these weights and based on the Markovian property of the process, we find, for \( t_1 < t_2 < t_3 < t_4 \),

\[
C_3(\tau_1, \tau_2, \tau_3) = \frac{1}{2} \sum_{i,j,k,l} P_{ij}^{-1}(\tau_1) P_{jk}^0(\tau_2) P_{kl}^1(\tau_3), \tag{11}
\]

where the summations are over all possible values of \( i = \pm, j = \pm, k = \pm, \) and \( l = \pm \).

We consider the other 23 time orderings in a similar way. We find only three types of pulses \( S(t) \) are needed for the definition of \( C_3(\tau_1, \tau_2, \tau_3) \). These pulses are presented in Table I together with the corresponding \( C_3(\tau_1, \tau_2, \tau_3) \). We then sum all the 24 contributions and use the convolution theorem of Laplace transform to arrive at the main result of this paper:

\[
\langle W^2 \rangle = \mathcal{L}^{-1} \left\{ \frac{\Omega^4 \epsilon^2}{16 \nu^2} \sum_{i,j,k,l} \left[ \hat{P}_{ij}^{-1}(u + u_+) \hat{P}_{j,k}^0(u) \hat{P}_{kl}^1(u + u_-) + \hat{P}_{ij}^{-1}(u + u_-) \hat{P}_{j,k}^0(u) \hat{P}_{kl}^1(u + u_+) + \hat{P}_{ij}^1(u + u_-) \hat{P}_{j,k}^0(u + \Gamma) \hat{P}_{kl}^1(u + u_-) + 2 \hat{P}_{ij}^1(u + u_+) \hat{P}_{j,k}^0(u + 2u_-) \hat{P}_{kl}^1(u + u_-) + CC \right] \right\}, \tag{12}
\]

where \( u = \Gamma/2 \pm i \omega_L, \mathcal{L}^{-1} \) denotes the inverse Laplace transform, and \( \hat{P}_{ij}^k(t) \) is the Laplace transform of \( P_{ij}^k(t) \). Using standard methods, we find the exact analytical expression for Mandel’s \( Q \) parameter, Eq. (5), based on Eq. (12) and \( \langle W \rangle \) [1.e., Eq. (7)] when \( T \to \infty \). It turns out that \( Q \) is not a simple model of the parameter; however, in certain limits, simple behavior is found.

Consider the slow modulation limit \( \nu \gg \Gamma \gg R \). Using our exact result, Eq. (12), we find

\[
Q \sim \frac{\xi}{2R} \left( 1 + e^{-2RT} \right) \left( \frac{(I_+ - I_-)^2}{2RT} \right), \tag{13}
\]

where \( I_\pm = \Omega^2 \Gamma \gamma_\Gamma + i (\omega_L \mp \nu)^2 / 4 \) are stationary solutions of the time-independent Bloch equation with frequency detuning \( \omega_L \mp \nu \), respectively. Similar to the line shape \( \langle I(\omega_L) \rangle \sim (I_+ - I_-)/2 \), \( Q \) in Eq. (13) exhibits splitting with two peaks at \( \omega_L = \pm \nu \). Unlike the line shape, \( Q \) depends on measurement time \( T \) and on \( R \). As an example, we choose the parameters \( \Gamma = 40 \text{ MHz}, \Omega = \Gamma/10, R = 1 \text{ s}^{-1}, \) and \( \omega_L = \nu = 1 \text{ GHz} \), which mimics a SM coupled to a slow two level system in a glass [6]; we find for \( RT \gg 1 \), \( Q = 2 \times 10^4 \xi \) which implies that fluctuations are very large (compared to the fast modulation limit soon to be considered). The

<table>
<thead>
<tr>
<th>( S(t) )</th>
<th>( C_3(\tau_1, \tau_2, \tau_3) )</th>
<th>Time order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1( \int_0^t \frac{1}{2} \sum P_{ij}^{-1}(\tau_1) P_{jk}^0(\tau_2) P_{kl}^1(\tau_3) )</td>
<td>1234i-4-2-3</td>
</tr>
<tr>
<td>2</td>
<td>0( \int_0^t \frac{1}{2} \sum P_{ij}^{-1}(\tau_1) P_{jk}^0(\tau_2) P_{kl}^1(\tau_3) )</td>
<td>2134i-3-2-1</td>
</tr>
<tr>
<td>3</td>
<td>0( \int_0^t \frac{1}{2} \sum P_{ij}^{-1}(\tau_1) P_{jk}^0(\tau_2) P_{kl}^1(\tau_3) )</td>
<td>2314i-3-2-1</td>
</tr>
</tbody>
</table>

The lengthy derivation of Eq. (13) is based on careful analysis of the poles of \( \langle W^2 \rangle \) and \( \langle W \rangle \) in Laplace domain. The result, Eq. (13), can be easily understood in the following way. The molecule can be found in two states up (+) and down (−). In the slow modulation limit, the rate of photon emission from these two states is determined by the stationary solution of the time independent Bloch equation, namely, \( I_\pm \), while transients are neglected. Using this physical picture, one can rederive Eq. (13) in a straightforward way. Equation (13) describes well the experiments in [2], where the second order correlation function \( g^{(2)}(t) \) was used to characterize the dynamics of a SM coupled to a two level system in a glass. To see the relation between these experiments and our work, we recall the relation [12,14],

\[
Q = \langle I(\omega_L) \rangle \left[ \frac{2}{T} \int_0^T dt_1 \int_0^t dt_2 g^{(2)}(t_2) - T \right]. \tag{14}
\]

For a slow process [2] \( g^{(2)}(t) = 1 + C \exp(-2RT) \) with \( C = (I_+ - I_-)/2(I_+ + I_-)^2 \), leading to agreement with Eq. (13). The question now remains whether one can go beyond this slow modulation limit and investigate faster processes based on SMS.
We therefore consider the fast modulation limit for which only the long measurement time $T$ limit is relevant (for this case $Q$ is independent of $T$). Mathematically different definitions of a fast modulation exist depending on the $R \to \infty$ limiting procedure used. Consider the case $R \to \infty$ keeping $\nu$ and $\Gamma$ fixed, which gives $Q = 0$. This is expected since in this case the bath is so fast the molecule cannot respond to it (e.g., the linewidth of the molecule is $\Gamma$). A more physically interesting case is to let $R \to \infty$ but keep the ratio $\Gamma_{eff}/\Gamma = \nu^2/(\Gamma R)$ finite. In this limit, the well-known line shape is Lorentzian with a width $\Gamma + \Gamma_{eff}$ and exhibits motional narrowing. Using our exact results, we find in the same limit and for $\omega_L = 0$ (i.e., at resonance),

$$Q = \frac{\xi 4 \Omega^2 \Gamma_{eff}^2}{\Gamma (\Gamma + \Gamma_{eff})^2 (\Gamma + 2 \Gamma_{eff})}.$$  \hspace{1cm} (15)

To estimate the magnitude of these fluctuations, we note that the maximum of $Q$ is found when $\Gamma_{eff} = \Gamma (1 + \sqrt{5})/2$ and then $Q = 0.36 \xi \Omega^2 / \Gamma^2$. Even if we take $|\Omega|/\Gamma = 0.1$ and $\xi = 5 \times 10^{-2}$ as a reasonable estimate for weak laser field and detection efficiency, we find a small value $Q = 1.8 \times 10^{-4}$. However, values of $|Q| \lesssim 5 \times 10^{-4}$ were reported in [14], so measurement in the fast modulation regime might be possible. However, other sources of fluctuations, mentioned in the introduction, must then be considered.

The fast modulation limit can be analyzed using a method developed by Loring and Mukamel [10] in the context of four wave mixing. Briefly, in this limit we use a factorization approximation $C_j(\tau_1, \tau_2, \tau_3) = C_1(\tau_1)C_1(\tau_2)C_1(\tau_3)$, and $C_1(\tau)$ is calculated based on standard line shape theory (details will be given elsewhere [21]). This approximation works well since correlation between the state of the molecule (i.e., $+, -$) during the one pulse interval [say $S(t) = 1$] with that of the following pulse interval [say $S(t') = 0$] is unimportant, because the bath is fast. Employing this approach, or using Eq. (12) directly, we find

$$Q \approx \begin{cases} 
\frac{\xi \Omega^2 \Gamma_{eff}}{2 (\omega_L^2 + \Gamma_{eff}^2/4)} & \Gamma_{eff} \ll \Gamma \\
\frac{\xi \Omega^2 \Gamma_{eff}^2}{(\omega_L^2 + \Gamma_{eff}^2/4)^2} & \Gamma_{eff} \ll \Gamma 
\end{cases} \hspace{1cm} (16)
$$

Equation (16) exhibits several interesting behaviors: (i) when $\Gamma_{eff} \ll \Gamma_{eff}$, a simple relation between the line shape and $Q$ holds, $Q = 2((\omega_L^2))/\Gamma$, and both exhibit motional narrowing; (ii) when $\Gamma_{eff} \ll \Gamma$, $Q \sim 1/R$, indicating that as the bath becomes faster the deviations from Poisson statistics become smaller (similar behavior is observed in the slow modulation limit); (iii) a dip in $Q$ is found when $\Gamma_{eff} \ll \Gamma$ [note that we have neglected $O(\Gamma_{eff}/\Gamma)^2$ terms which give corrections at $\omega_L = 0$].

In conclusion, the three time correlation function describes line shape fluctuations, characterized by $Q$. Similar correlation functions describe also ensemble nonlinear spectroscopies, which elucidate complicated dynamical processes in systems with strong inhomogeneous line broadening. In SMS, inhomogeneous line broadening is absent; however, time-dependent fluctuations are present. The analysis of these fluctuations yields detailed information on the underlying stochastic events, information which is not accessible when an ensemble of molecules is considered.

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[20] The weights are $P^R_{ij}(t) = (1/2)[1 + (-1)^{i+j} \exp(-2Rt)]$, $P^R_{ij}(t) = R \exp(-Rt) \sin(Y(t)/Y_1) \sin(Y(t)/Y_1)$, $P^R_{ij}(t) = \exp(-Rt) \cos(Y(t)/Y_1)$, $P_{ij}^R(t) = CC \times P_{ij}^R(t)$, and $Y_1 = \sqrt{v^2 - R^2}$. $P_{ij}^{R^2}(t)$ is given by $P_{ij}^{R^2}(t)$ when $v$ is replaced with $2v$.