Probing Dynamics of Single Molecules: Non-linear Spectroscopy Approach

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A two level model of a single molecule undergoing spectral diffusion dynamics and interacting with a sequence of two short laser pulses is investigated. Analytical solution for the probability of \( n = 0, 1, 2 \) photon emission events for the telegraph and Gaussian processes are obtained. We examine under what circumstances the photon statistics emerging from such pump-probe set up provides new information on the stochastic process parameters, and what are the measurement limitations of this technique. The impulsive and selective limits, the semiclassical approximation, and the fast modulation limit, exhibit general behaviors of this new type of spectroscopy. We show, that in the fast modulation limit, where one has to use impulsive pulses in order to obtain meaningful results, the information on the photon statistics is contained in the molecule’s dipole correlation function, equivalently to continuous wave experiments. In contrast, the photon statistics obtained within the selective limit depends on the both spectral shifts and rates and exhibits oscillations, which are not found in the corresponding line-shape.

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I. INTRODUCTION

Recently van Dijk et al [1] reported the first experimental ultra-fast pump-probe study of a single molecule system. Unlike previous approaches to non-linear spectroscopy where only the ensemble average response to the external fields is resolved [2], the new method yields direct information on single molecule dynamics, gained through the analysis of photon statistics. Although the original experiment [1] was conducted on a molecule undergoing a relatively simple relaxation process, the potential of combining non-linear spectroscopy with single molecule spectroscopy inspires many unanswered questions: What are the limitations of the investigation of fast dynamics? How does the information contained in these experiments differ from the information contained in simpler continuous wave experiments? How to design the external control fields, so that needed information on dynamics of molecules is gained? What is the fingerprint of coherence in these types of experiments, and how its influence on photon statistics is suppressed due to dephasing processes? The answers to these questions are important for better understanding of a wide variety of physical phenomena and have implication in the investigation of ultra-fast dynamics of molecules in the condensed phase, of quantum properties of light, and in the field of quantum information and computation [1–3, 4, 5, 6, 7, 8, 9, 10]. Here we present a treatment based on the stochastic Kubo-Anderson model [2, 10, 11, 12], which yields general insights on the problem.

We consider a sequence of two identical laser pulses interacting with a single molecule (or an atom, or a quantum dot) undergoing a spectral diffusion process, namely a molecule whose absorption frequency is randomly modulated in time due to interaction with a thermal bath. The electronic states of the single emitter are modeled based on the two level system approximation. Most single molecules have a triplet state, however the life time of the triplet is much longer than the time scales under consideration in this paper, and it can be neglected. It is assumed that the pulses are very short compared with the inverse rate \( R \) of the spectral diffusion process, as well as with the inverse of the radiative life-time of the emitter, \( \Gamma \). The probability of photon emissions during the pulse event is then negligible, and a pair of pulses yields two photons at most. Repeating the experiment many times one obtains the probabilities \( \langle P_0 \rangle, \langle P_1 \rangle \) and \( \langle P_2 \rangle \) of emitting 0, 1 and 2 photons, where \( \langle \cdots \rangle \) designates the average over the stochastic modulation of the two level system’s absorption frequency \( \omega(t) \). In what follows we generalize the results obtained in our earlier publication [12] by:

(i) establishing the general expressions for \( \langle P_0 \rangle, \langle P_1 \rangle \) and \( \langle P_2 \rangle \) in the limit of long measurement times without any restricting assumptions regarding the laser detuning,

(ii) comparing the photon statistics obtained for the two state Kubo-Anderson and Gaussian processes.

We show, that under certain conditions this type of photon statistics reveals important information on single molecule dynamics, information which might be difficult to obtain using other theoretical approaches to single molecule spectroscopy [13, 14, 15, 16, 17, 18, 19, 20, 21]. The general expressions for the photon statistics are obtained starting with the path interpretation of Mollow and Zoller, Marte and Walls [22, 23] of the optical Bloch equations [24]. We show, that depending on the characteristics of the stochastic dynamics and the laser field parameters, different types of non-linear spectroscopies emerge. In particular, sensitivity to the phase accumulated by the system in the delay interval between the pulses is found, and impulsive and selective type of spectroscopies are considered in detail. The Kubo-Anderson spectral diffusion process [10] used in this work is found in many molecular systems [14, 19, 20, 21] and may be easily detected, when the process is slow by means of the spectral trail technique. Our goal is developing gen-
The operator ing electromagnetic field through $\Omega$ is described by the density matrix, represented by the off-diagonal matrix elements of the density matrix. For the sake of mathematical convenience we use $\sigma_{ee}$ and $\sigma_{gg}$ to describe the coherences, namely the off-diagonal matrix elements of the density matrix. For the sake of mathematical convenience we use the following 4-dimensional basis $|e⟩ = (1, 0, 0, 0)^T$ and $|g⟩ = (0, 1, 0, 0)^T$ for the excited and ground states respectively and $|e⟩$, $|g⟩$ describe the coherences, namely the off-diagonal matrix elements of the density matrix. For the sake of mathematical convenience we use the following 4-dimensional basis $|e⟩ = (1, 0, 0, 0)^T$, which means that the system is in the pure excited state, $|g⟩ = (0, 1, 0, 0)^T$ - the ground state, and $|e⟩ = (0, 0, 1, 0)^T$ and $|e⟩^* = (0, 0, 0, 1)^T$ describe the coherences. The dynamical evolution of the density matrix in the presence of the external laser field is given by the optical Bloch equation [14]:

$$\dot{\sigma} = L(t) \sigma + \dot{\Gamma} \sigma. \quad (1)$$

The operator

$$L(t) = \begin{pmatrix} -\Gamma & 0 & -i\Omega f(t) & i\Omega f(t) \\ 0 & 0 & -i\Omega f(t) & i\Omega f(t) \\ -i\Omega f(t) & -i\Omega f(t) & i\omega(t) - \Gamma/2 & 0 \\ -i\Omega f(t) & -i\Omega f(t) & 0 & -i\omega(t) + \Gamma/2 \end{pmatrix}$$

(2)

describes the interaction of the system with the driving electromagnetic field through $\Omega f(t)$, where $\Omega = -(1/h)d_{ge} \cdot E_0$ is the Rabi frequency with $E_0$ - the amplitude of the electric field and $d_{ge} = d_{eg}$ the transition dipole moment of the two level system. The operator $\Gamma = \Gamma|g⟩⟨e|$ describes the transition from the excited state into the ground state, due to spontaneous emission with $\Gamma$ designating the emission rate. Finally $\omega(t)$ is the stochastic time dependent absorption frequency of the system. The spectral diffusion process $\omega(t)$ is modeled using the Kubo-Anderson approach:

$$\omega(t) = \omega_0 + \delta w(t), \quad (3)$$

where $\omega_0$ is the bare absorption frequency of the single emitter, and $\delta w(t)$ is a random function of time [2, 10]. We will assume the process $\delta w(t)$ is stationary, its mean is zero, its correlation function is

$$\langle \delta w(t_0 + t)\delta w(t_0) \rangle = \nu^2 \psi(t), \quad (4)$$

where $\psi(0) = 1$ and $\psi(\infty) = 0$. Later we will demonstrate our results for a particular choice

$$\psi(t) = e^{-2\nu T}, \quad (5)$$

obtaining semi-analytical solutions for the Gaussian process and analytical solution for the two-state Kubo-Anderson process [14, 27], where $\omega(t) = \omega_0 + \nu$ or $\omega(t) = \omega_0 - \nu$, with the rate $R$ determining the transition between the $+$ and $-$ states. The later is used to model single molecules in low temperature glasses [21].

In the case of two identical square pulses the modulating function $f(t)$ in Eq. (2) is:

$$f(t) = \begin{cases} \cos(\Omega_L t) & 0 < t < t_1 \\
0 & t_1 < t < t_2 \\
\cos(\Omega_L (t - t_2)) & t_2 < t < t_3 \\
0 & t_3 < t \end{cases}, \quad (6)$$

where $\Omega_L$ is the laser frequency, $t_1 = t_3 - t_2 = T$ is the pulses duration, and $\Delta = t_2 - t_1$ is the delay between the pulses. In our calculations we assume: (i) that the system is always found in its ground state at the beginning of the experiment. (ii) In order to get meaningful measurable results one has to use sufficiently intense laser fields such that $\Omega T \sim 1$ - weak fields cannot excite the emitter even once. (iii) The pulses are short enough, so that the lifetime of the excited state is much longer than pulse’s duration - $\Gamma T \ll 1$ (hence, $\Omega \gg \Gamma$).

(iv) The rate $R$ of changes of the stochastic process $\omega(t)$ satisfies $RT \ll 1$ (hence, $\Omega \gg R$). Assumption (iii) leads to the mentioned negligibility of photon emissions during the pulse events. The last assumption implies, that the time-dependent absorption frequency $\omega(t)$ is unchanged during the excitations, and will be taken to be $\omega(t_1) = \omega_0 + \delta w(t_1)$ during the first pulse event and $\omega(t_2) = \omega_0 + \delta w(t_2)$ during the second pulse event.

A calculation given in short in Appendix A yields the following expression for the probabilities of emitting zero, one and two photons in the limit of long measurement times $t \to \infty$ for a particular realization of the stochastic process $\omega(t)$:
\[ P_n[\omega(t_1), \omega(t_2), \theta(\Delta)] = P^n_{\text{Cl}}[\omega(t_1), \omega(t_2)] + 2e^{-\frac{\Delta \omega}{2}} \text{Re} \left\{ A^n_{\text{coh}}[\omega(t_1), \omega(t_2)] e^{i(\theta(\Delta) + \omega_0(T + \Delta))} \right\}, \tag{7} \]

where \( \theta(\Delta) \) is the random phase accumulated during the delay interval given by

\[ \theta(\Delta) = \int_0^\Delta \delta w(t) \, dt, \tag{8} \]

and \( P^n_{\text{Cl}}[\omega(t_1), \omega(t_2)] \) and \( A^n_{\text{coh}}[\omega(t_1), \omega(t_2)] \) are given in Table 1, where \( G[\omega(t_i)] \) \( (i = 1, 2) \) is the Green function defined in Eqs. (9, 10) below. Note, from Eq. (7) it follows that all accumulated random phase effects become negligible when \( \Gamma \Delta \gg 1 \). The two summands in Eq. (7) describe two kinds of possible quantum trajectories leading to required number of photon emission events: the term \( P^n_{\text{Cl}}[\omega(t_1), \omega(t_2)] \) we call semiclassical in the sense that it summarizes the paths where at the beginning of the delay the system is found in one of the pure states \(|e\rangle\) or \(|g\rangle\). For example, consider the first term of \( P^n_{\text{Cl}} \); the system starts in the electronic ground state \(|g\rangle\), then it evolves with the propagator of the first pulse \( G[\omega(t_1)] \) without photon emissions and reaches the excited state \(|e\rangle\), it stays in the excited state during the delay interval (with probability \( e^{-\Gamma \Delta} \)), and afterwards the second pulse with the propagator \( G[\omega(t_2)] \) stimulates the induced emission, bringing the system back to the ground state \(|g\rangle\) without emitting a photon. The second summand in the right-hand side of Eq. (7), \( A^n_{\text{coh}}[\omega(t_1), \omega(t_2)], \) summarizes the contribution of the coherence effects (i.e. all those quantum paths where at the beginning of the delay interval the system is left in a superposition of the pure states). It can be shown (see Appendix A), that very strong or resonant \( \pi \)-pulses, where \( \Omega T = \pi \), simply switch the state of the molecule being in \(|g\rangle\) to \(|e\rangle\) or vice versa. Hence, they do not excite the coherence - in such cases the coherent term \( A^n_{\text{coh}}[\omega(t_1), \omega(t_2)] \) vanishes.

| \( n \) | \( P^n_{\text{Cl}}[\omega(t_1), \omega(t_2)] \) | \( A^n_{\text{coh}}[\omega(t_1), \omega(t_2)] \) |
|---|---|---|
| 0 | \(|g|G[\omega(t_2)]e\rangle\langle e|G[\omega(t_1)]|g\rangle e^{-\Gamma \Delta} + \langle g|G[\omega(t_2)]|g\rangle\langle g|G[\omega(t_1)]|g\rangle \) | \(|g|G[\omega(t_2)]|e\rangle\langle e|G[\omega(t_1)]|g\rangle \) |
| 1 | \(|g|G[\omega(t_2)]|g\rangle\langle g|G[\omega(t_1)]|g\rangle + \langle g|G[\omega(t_2)]|g\rangle\langle g|G[\omega(t_1)]|g\rangle \) | \(|e|G[\omega(t_2)]|e\rangle\langle e|G[\omega(t_1)]|g\rangle \) |
| 2 | \(|e|G[\omega(t_2)]|g\rangle\langle e|G[\omega(t_1)]|g\rangle \) \((1 - e^{-\Gamma \Delta})\) | 0 |

**Table 1:** Photon statistics for two short pulses and arbitrary spectral diffusion process \( \omega(t) \).

In Table 1 the propagator of the two level system during the first and the second pulse events \( G[\omega(t_1)] \) \( (i = 1, 2) \) is obtained within the rotating wave approximation (RWA) (see Appendix A):

\[ G[\omega(t_i)] = e^{T_i L^{\text{RWA}}[\omega(t_i)]}, \tag{9} \]

where

\[ L^{\text{RWA}}[\omega(t_i)] = \begin{pmatrix} 0 & 0 & -\Omega & i\Omega \\ 0 & 0 & 0 & -\Omega \\ -\Omega & i\Omega & 0 & i\delta(t_i) \\ i\Omega & -i\Omega & i\delta(t_i) & 0 \end{pmatrix}, \tag{10} \]

and

\[ \delta(t_i) = \delta_L - \delta w(t_i), \tag{11} \]

with

\[ \delta_L = \omega_L - \omega_0 \tag{12} \]

is the detuning. The mathematical calculations were made with the help of Mathematica 5.0. Evidently, since the spontaneous emissions during the pulse events are neglected (\( \Omega \gg \Gamma \)), the Green function Eq. (4) describes well-known Rabi oscillations.

**III. INFLUENCE OF SPECTRAL DIFFUSION ON PHOTON STATISTICS.**

We now take the average of \( P_n[\omega(t_1), \omega(t_2), \theta(\Delta)] \) Eq. (7) over the stochastic process \( \omega(t) \). This procedure requires the knowledge of the joint probability density function (PDF) \( \mathcal{P}[\omega(t_1), \omega(t_2), \theta(\Delta)] \) of finding the system’s absorption frequency \( \omega(t) \) in the infinitesimal range near \( \omega_0 + \delta \omega(t_1) \) at \( t_1 \), near \( \omega_0 + \delta \omega(t_2) \) at \( t_2 \), with accumulated random phase \( \theta(\Delta) \). Then by definition the
average of $P_n$ is:

$$
\langle P_n \rangle = \int_{-\infty}^{\infty} d\theta(\Delta) \int_0^\infty d\omega(t_1) \int_0^\infty d\omega(t_2) \times
$$

$$
\times P_n[\omega(t_1), \omega(t_2), \theta(\Delta)] P[\omega(t_1), \omega(t_2), \theta(\Delta)].
$$

Later we find exact solution for the three-variable PDF $P[\omega(t_1), \omega(t_2), \theta(\Delta)]$ for the case of two-state Kubo-Anderson process, thus providing all essential tools for calculation of $\langle P_n \rangle$ in the case of the telegraph noise. But first, we discuss several limiting cases common for all stationary processes.

In Fig. 2 we plotted the probability of transition from the ground to the excited state $\langle \epsilon | \mathcal{G}(\omega(t_1)) | g \rangle$ Eq. (54) for two identical π-pulses. The smooth and the dashed curves represent $\langle \epsilon | \mathcal{G}(\omega(t_1)) | g \rangle$ as a function of $\delta_L$ for $\omega(t) = \omega_0 + \nu$ with $\nu = \Omega$. The figure illustrates that since the two curves practically do not overlap for $\nu \gtrsim \Omega$ the probabilities to excite the molecule during the first pulse event and in the state $\omega(t_2) = \omega_0 - \nu$ during the second pulse event are measurable different.

Impulsive limit $\Omega \gg \nu$. - In the limit $\Omega \gg \nu$, which we call impulsive, the matrix elements of $\mathcal{G}(|\omega(t_1)\rangle)$ and $\mathcal{G}(|\omega(t_2)\rangle)$ Eqs. (54) become independent of the value of stochastic detuning $\delta \omega(t)$ at the moment of the excitation. Thus instead of the multi variable PDF $P[\omega(t_1), \omega(t_2), \theta(\Delta)]$ we now have to deal only with the one variable PDF of the phase $\theta(\Delta)$. As a result the photon statistics shows an interesting relation with linear continuous wave spectroscopy:

$$
\lim_{\Omega \gg \nu} \langle P_n \rangle = \lim_{\Omega \gg \nu} P_n^{\text{Cl}}_{\nu} + 2 e^{-\frac{\pi^2}{\Omega^2}} \Re \left[ \phi(\Delta) e^{i\omega_0(T + \Delta)} \right] \lim_{\Omega \gg \nu} A_n^{\text{Coh}},
$$

where using Table 1 and Eqs. (55-16):

$$
\lim_{\Omega \gg \nu} \langle P_1^{\text{Cl}} \rangle = \frac{2\Omega^2 [ \delta_L^2 + \Omega^2 \cos^2 \left( \frac{i\Omega T}{2} \sqrt{1 + \frac{\delta_L^2}{\Omega^2}} \right) ] \sin^2 \left( \frac{i\Omega T}{2} \sqrt{1 + \frac{\delta_L^2}{\Omega^2}} \right)}{(\delta_L^2 + \Omega^2)^2},
$$

$$
\lim_{\Omega \gg \nu} \langle P_2^{\text{Cl}} \rangle = \frac{(1 - e^{-\Gamma \Delta}) \Omega^4 \sin^4 \left( \frac{i\Omega T}{2} \sqrt{1 + \frac{\delta_L^2}{\Omega^2}} \right)}{(\delta_L^2 + \Omega^2)^2},
$$

$$
\lim_{\Omega \gg \nu} \langle P_0^{\text{Cl}} \rangle = 1 - \lim_{\Omega \gg \nu} \langle P_1^{\text{Cl}} \rangle - \lim_{\Omega \gg \nu} \langle P_2^{\text{Cl}} \rangle
$$

and

$$
\lim_{\Omega \gg \nu} A_n^{\text{Coh}} = \frac{\Omega^2 \left( 2\delta_L \sin^2 \left( \frac{i\Omega T}{2} \sqrt{1 + \frac{\delta_L^2}{\Omega^2}} \right) + i \frac{\delta_L^2}{\Omega} \cos \left( \frac{i\Omega T}{2} \sqrt{1 + \frac{\delta_L^2}{\Omega^2}} \right) \right) \left( \delta_L^2 + \Omega^2 \right)^2}{4 (\delta_L^2 + \Omega^2)^2}.
$$

In Eq. (14) the function $\phi(\Delta)$ given by

$$
\phi(\Delta) = \langle \exp[i\theta(\Delta)] \rangle = \langle \exp[i \int_0^\Delta \delta \omega(t) dt] \rangle
$$

is the well investigated Kubo-Anderson correlation.
function, whose Fourier transform is the line shape of the two level system according to the Wiener-Khintchine theorem. In conclusion, we see, that working with very strong laser fields \( \Omega \gg \nu \) under assumptions (iii,iv) we gain the same information as found in the line-shape in continuous wave experiments.

Near the resonance, where \( \delta_L \sim 0 \), using Eqs. (14)-(18) we find
\[
\lim_{\Omega \gg \nu} \langle P_0 \rangle = e^{-\Gamma\Delta} \sin^4 \left( \frac{\Omega T}{2} \right) + \cos^4 \left( \frac{\Omega T}{2} \right) - \frac{1}{2} e^{-\Gamma\Delta/2} \sin^2 (\Omega T) \text{Re} \left[ \phi(\Delta) e^{i\omega_0(T+\Delta)} \right],
\]
(20)
\[
\lim_{\Omega \gg \nu} \langle P_1 \rangle = \frac{1}{2} \sin^2 (\Omega T) \left\{ 1 + e^{-i\Delta} \text{Re} \left[ \phi(\Delta) e^{i\omega_0(T+\Delta)} \right] \right\},
\]
(21)
\[
\lim_{\Omega \gg \nu} \langle P_2 \rangle = (1 - e^{-\Gamma\Delta}) \sin^4 \left( \frac{\Omega T}{2} \right).
\]
(22)

From Eqs. (20)-(21) we see, that for the strong \( \pi \)-pulses the coherent terms vanish, as mentioned. In contrast, for \( \pi/2 \)-pulses with \( \Omega T = \pi/2 \) the importance of the coherent terms, and hence, the correlation function \( \phi(\Delta) \) on the photon statistics is the strongest, since the \( \pi/2 \) pulse excites the off diagonal terms of the pulse-propagators \( G(\omega(t_1)) \) Eq. (5) [25].

Semiclassical approximation. - The influence of the coherence on photon statistics in many experimental cases is expected to be difficult to detect. It may be because of the dephasing effects caused by the damping coefficient \( e^{-\Gamma t} \) multiplying the coherent terms \( A_n^{\text{coh}} \) in Eq. (7). Moreover, because of the large value of the bare optical transition frequency \( \omega_0 \) the coherent paths oscillate too fast to be detected (see the term \( e^{i\omega_0(T+\Delta)} \) in Eq. (7)). In such cases a practical approximation is to keep only the semiclassical terms \( P_n^{\text{Cl}} \). Nevertheless, we stress, that for multilevel systems or in non optical experiments on Josephson junction coherence contribution is important [8]. Since the semiclassical paths are independent of \( \langle P_n^{\text{Cl}} \rangle \) we need only the marginal, two dimensional PDF \( \mathcal{P}[\omega(t_1), \omega(t_2)] \). For example, in the case of Gaussian noise \( \mathcal{P}[\omega(t_1), \omega(t_2)] \) we have:
\[
\mathcal{P}[\delta w(t_1), \delta w(t_2)] = \frac{1}{2\pi\nu^2\sqrt{1-\psi^2}} \times \\
\exp \left[ -\frac{\delta w(t_1)^2 + \delta w(t_2)^2 - 2\delta w(t_1)\delta w(t_2)\psi}{2\nu^2(1-\psi^2)} \right],
\]
(23)
where \( \psi = \psi(|t_2-t_1|) \) is the time dependent part of the correlation function in Eq. (4). Once the two-time PDF \( \mathcal{P}[\omega(t_1), \omega(t_2)] \) is known, \( \langle P_n \rangle \) within the semiclassical approximation is:
\[
\langle P_n^{\text{Cl}} \rangle = \int_0^{\infty} \int_0^{\infty} \mathcal{P}_n^{\text{Cl}}[\omega(t_1), \omega(t_2)] \mathcal{P}[\omega(t_1), \omega(t_2)] d\omega(t_1) d\omega(t_2).
\]
(24)
In Appendix B we give the explicit semiclassical approximation for the two state Kubo-Anderson model Eqs. (55)-(57). Later in Fig. 3 we compare these results with similar results for the Gaussian noise, which was solved semi-analytically with the help of Mathematica 5.0. In both calculations the same correlation function Eqs. (44) [44] was used.

IV. TWO STATE PROCESS: EXACT SOLUTION

Now we obtain the exact solution for the two state Kubo-Anderson Poissonian process, where the absorption frequency of the system jumps between the + and − states, i.e. \( \omega(t) = \omega_0 \pm \nu \). We denote the initial state, during the first pulse with \( \omega(t_1) = + \) or \( \omega(t_1) = - \). Similarly, the final state at the second pulse is \( \omega(t_2) = + \) or −. Since the random phase is now given by \( \Delta = \nu(T^+ - T^-) \), where \( T^\pm \) are occupation times in states + and −, obeying \( \Delta = T^+ + T^- \), the joint PDF \( \mathcal{P}[\omega(t_1), \omega(t_2), \theta(\Delta)] \) can be found from the joint PDF \( \mathcal{P}[\omega(t_1), \omega(t_2), T^+] \) of finding the system in state \( \omega(t_1) = \pm \) during the first pulse, state \( \omega(t_2) = \pm \) during the second and with the occupation time \( T^+ \) between the two pulses. In this case, where the random process takes only discrete values, \( \langle P_n \rangle \) Eq. (13) takes the form
\[
\langle P_n \rangle = \sum_{\omega(t_1), \omega(t_2) = \pm} \mathcal{P}[\omega(t_1), \omega(t_2)] P_n^{\text{Cl}}[\omega(t_1), \omega(t_2)] + 2 \text{Re} \left\{ e^{i\omega_0(T+\Delta)} - \frac{e^{i\Delta}}{2} A_n^{\text{coh}}[\omega(t_1), \omega(t_2)] \int_0^{\infty} e^{i\nu(2T^+-\Delta)} h[\omega(t_1), \omega(t_2), T^+] dT^+ \right\},
\]
(25)
where
\[
\mathcal{P}[\pm, \pm] = \frac{1 + e^{-2R\Delta}}{4}, \quad \mathcal{P}[\pm, \mp] = \frac{1 - e^{-2R\Delta}}{4}
\]
(26)
are the probabilities of finding the particle initially in state $\omega(t_1) = \pm$ and finally in state $\omega(t_2) = \pm$, which are easy to obtain from Poissonian statistics. In the integrand of Eq. (25) one can recognize Laplace transform $T^+ \rightarrow -2i\nu$ of $\hbar [\omega(t_1), \omega(t_2), T^+]$. Simple rearrangement leads to:

$$
\langle P_n \rangle = \sum_{\omega(t_1), \omega(t_2) = \pm} \mathcal{P}[\omega(t_1), \omega(t_2)] P_n^{\text{Cla}}[\omega(t_1), \omega(t_2)] + 2 \text{Re} \left\{ e^{-\frac{\hbar}{2i} \omega(t_2) \Delta + i\omega t} \hbar [\omega(t_1), \omega(t_2), -2i\nu] A_n^{\text{Coh}}[\omega(t_1), \omega(t_2)] \right\},
$$

(27)

where $\hbar [\omega(t_1), \omega(t_2), -2i\nu]$ is the Laplace $T^+ \rightarrow -2i\nu$ transform of $\hbar [\omega(t_1), \omega(t_2), T^+]$. The procedure of derivation of $\hbar [\omega(t_1), \omega(t_2), -2i\nu]$, based on the renewal processes theory [27, 29], is given in detail in Appendix C. Here we present the final results:

$$
\hbar [\pm, \pm, -2i\nu] = e^{-\Delta(R + i\nu)} \left[ \cosh \left( \Delta \sqrt{R^2 - \nu^2} \right) \pm \frac{i\nu \sinh \left( \Delta \sqrt{R^2 - \nu^2} \right)}{\sqrt{R^2 - \nu^2}} \right],
$$

(28)

$$
\hbar [\mp, \pm, -2i\nu] = e^{-\Delta(R + i\nu)} \frac{\sinh \left[ \Delta \sqrt{R^2 - \nu^2} \right]}{2\sqrt{R^2 - \nu^2}}.
$$

(29)

Using Eqs. (20, 29) and Table 1 the calculation of $\langle P_n \rangle$ is straightforward.

**Semiclassical selective limit.** Now we consider selective limit for the two state Kubo-Anderson process within the semiclassical approximation. From the exact solution Eqs. [30, 38], considering two opposite situations $\Omega \sim \delta_L + \nu$ and $\Omega \ll \delta_L - \nu$ or $\Omega \sim \delta_L - \nu$ and $\Omega \ll \delta_L + \nu$ we find:

$$
\langle \lim_{\nu \gg \Omega} P_n^{\text{Cla}} \rangle = \frac{(1 + e^{-2R\Delta}) \Omega^2 \sin^2 \left( \frac{\Omega T}{2} \sqrt{1 + \frac{(|\delta_L| - \nu)^2}{\nu^2}} \right)}{2 \left[ (|\delta_L| - \nu)^2 + \Omega^2 \right]} \times \frac{(|\delta_L| - \nu)^2 + \Omega^2 \cos^2 \left( \frac{\Omega T}{2} \sqrt{1 + \frac{(|\delta_L| - \nu)^2}{\nu^2}} \right)}{(|\delta_L| - \nu)^2 + \Omega^2} + \frac{(1 - e^{-2R\Delta}) \Omega^2 \sin^2 \left( \frac{\Omega T}{2} \sqrt{1 + \frac{(|\delta_L| - \nu)^2}{\nu^2}} \right)}{2 \left[ (|\delta_L| - \nu)^2 + \Omega^2 \right]},
$$

(30)

$$
\langle \lim_{\nu \gg \Omega} P_0^{\text{Cla}} \rangle = 1 - \langle \lim_{\nu \gg \Omega} P_1^{\text{Cla}} \rangle - \langle \lim_{\nu \gg \Omega} P_2^{\text{Cla}} \rangle.
$$

(31)

Notice, that $P_1^{\text{Cla}}$ depends on $\Delta$ only through $e^{-2R\Delta}$. Hence, using Eq. (31) it is easy to measure the dynamics of the molecule.

When $\delta_L = \pm \nu$ from Eqs. (30, 32) we find:

$$
\lim_{|\delta_L| = \nu \gg \Omega} \langle P_1^{\text{Cla}} \rangle = \frac{1 + e^{-2R\Delta}}{8} \sin^2 \left( \Omega T \right) + \frac{1 - e^{-2R\Delta}}{2} \sin^2 \left( \frac{\Omega T}{2} \right),
$$

(33)

$$
\lim_{|\delta_L| = \nu \gg \Omega} \langle P_2^{\text{Cla}} \rangle = \frac{(1 + e^{-2R\Delta})(1 - e^{-\Gamma\Delta}) \Omega^4}{4 \left[ (|\delta_L| - \nu)^2 + \Omega^2 \right]^4},
$$

(34)

Note, that Eqs. (33, 34) exhibit Rabi oscillations. Applying Eqs. (33, 34) to the $\pi$-pulses gives:

$$
\lim_{|\delta_L| = \nu \gg \Omega} \langle P_1^{\text{Cla}} \rangle = \frac{1}{2} \left( 1 - e^{-2R\Delta} \right),
$$

(35)

$$
\lim_{|\delta_L| = \nu \gg \Omega} \langle P_2^{\text{Cla}} \rangle = \frac{1}{4} \left( 1 + e^{-2R\Delta} \right) \left( 1 - e^{-\Gamma\Delta} \right),
$$

(36)

and

$$
\lim_{|\delta_L| = \nu \gg \Omega} \langle P_0^{\text{Cla}} \rangle = \frac{1}{4} \left( 1 + e^{-2R\Delta} \right) \left( 1 + e^{-\Gamma\Delta} \right).
$$

(37)
The results of Eqs. (35-37) make perfect physical sense. For example a single photon may be emitted only if the absorption frequency $\omega(t)$ is found once in the + state and once in the − state, since only one of these states is in resonance with the laser. The system, which is in the ground state at the beginning of the experiment, gets excited exactly once, and nothing interrupts the spontaneous emission process. Hence, $\langle P_1 \rangle = \mathcal{P}[-,+] + \mathcal{P}[-,+]$. Note, that for the strong $\pi$-pulses in the case of the impulsive limit we have $\langle P_1 \rangle = 0$ (see Eq. (21)).

V. DEMONSTRATION OF RESULTS

In Fig. 3 we plotted the semiclassical parts of $\langle P_0 \rangle$, $\langle P_1 \rangle$ and $\langle P_2 \rangle$ for the two state and Gaussian processes for two identical $\pi$-pulses. We see the transition from the selective limit (first row) to the impulsive limit (third row), where the graphs corresponding to the two processes visually coincide. The graphs in Fig. 3 clearly provide the information on the spectral shifts $\nu$. Finally, it is worth noticing, that the behavior of photon statistics corresponding to the two-state process is oscillatory in $\delta_L$, while in the case of the Gaussian noise it is not. The origin of this effect follows from the fact, that the matrix elements of the propagators $\mathcal{G} [\omega(t)]$ Eqs. (35-37), and hence the probability of $n$ photon emission events, $P_n$ are sinusoidal functions of $\delta_L - \delta \omega(t)$. Therefore in the case of discrete dichotomic noise the phase of the sinusoidal functions we are summing up takes only two values $\pm \nu$. However, in the case of the continuous Gaussian distribution we integrate over a continuous range of phases. Thus, as we approach the selective limit in the case of Gaussian noise, the oscillations in $\delta_L$ are
cases may occur:

implies $\Omega \gg R$.

the case of pure resonance with the $+\text{ state}$ $R$ measure

the dynamical information on the rate $= 3\Gamma$, $\Gamma = 1$ (hence, $R \pi$) the case of two $\delta$-pulses with $\Omega = 60\Gamma$, $R = 3\Gamma$. The lower graph is the contourplot of the upper three-dimensional graph.

destroyed by averaging.

In Fig. 4 we plotted the three dimensional (above) and contour (below) graphs of $(P_1^{\text{Cl}})$ for the two state Kubo-Anderson process as a function of the delay $\Delta$ and spectral shift $\nu$ in the case of pure resonance with the $+\text{ state}$ $\delta_L = \nu$ for two identical $\pi$-pulses with $\Omega = 60\Gamma$, $R = 3\Gamma$. The lower graph is the contourplot of the upper three-dimensional graph.

A. Measurement Limitations

Combining the requirements $\Omega \Delta \sim 1$ and $RT \ll 1$ implies $\Omega \gg R$. Hence, only the three following limiting cases may occur:

(a) $\Omega \gg \nu \gg R$ – impulsive pulse, slow process
(b) $\Omega \gg R \gg \nu$ – impulsive pulse, fast process
(c) $\nu \gg \Omega \gg R$ – selective pulse, slow process, while all the other combinations violate our assumptions.

As mentioned, the direct dependence of the photon statistics on the shift $\nu$ and the rate $R$ becomes undetectable when the strength of the laser field reaches the impulsive limit. We saw (see Fig. 2), that for $\nu \leq \Omega$ the information on the stochastic process encoded in photon statistics becomes equivalent to the information provided by line-shape in continuous wave spectroscopy. Since $\Omega \gg R$ we see, that the effectiveness of the pump-probe technique is restricted to slow processes $\nu \gg R$. Thus, the assumptions $RT \ll 1$ and $\Omega T \sim 1$ determine the limitations of the measurement of stochastic dynamics, and to get information on wider range of dynamics our method must be improved by removing these conditions. In our future work we plan to focus on the investigation of processes, where $RT \ll 1$ is not fulfilled.

VI. FAST MODULATION

Finally, let us consider an interesting case of the fast modulation limit $R \to \infty$, $\nu \to \infty$ such that $R \gg \nu$, where the motional narrowing effects take place. From inequalities $a, b, c$ follows, that the fast modulation limit must be impulsive limit as well. Therefore, Eqs. (2) hold with

$$\lim_{R \gg \nu} \phi(\Delta) = \exp(-\Gamma_{\text{SD}}\Delta/2), \quad (38)$$

with

$$\Gamma_{\text{SD}} = \nu^2/R, \quad (39)$$

which means that $(\Gamma_{\text{SD}} + \Gamma)/2$ is the renormalized decay rate which damps the coherent terms. Note, that $\Gamma_{\text{SD}}$ is a measurable physical observable determining the width of the line shape in continuous wave spectroscopy [10].

The results of Eq. (38) are obtained straightforwardly for the two state Kubo-Anderson process using our exact solution Eqs. (28,29). We calculate the limit $R \gg \nu$ in such a way, that $\Gamma_{\text{SD}} = \nu^2/R$ is finite. For example considering Eq. (29) we have:

$$\hat{h}[\mp, \pm, -2i\nu] = e^{-\Delta(R-\nu)} \frac{\sinh(\Delta \sqrt{R^2 - \nu^2})}{2\sqrt{R^2 - \nu^2}} \approx e^{-\Delta(R-\nu)/4} \left(e^{R\Delta \sqrt{1 - \nu^2/R^2}} - e^{-R\Delta \sqrt{1 - \nu^2/R^2}}\right) \quad (40)$$

Using $\sqrt{1 - \nu^2/R^2} \sim 1 - \nu^2/4R^2$ in the exponent of Eq. (40) we obtain:

$$\lim_{R \gg \nu} \hat{h}[\mp, \pm, -2i\nu] = \lim_{R \gg \nu} \frac{e^{-\Delta(R-\nu)/4}}{4} \left(e^{R\Delta(1-\nu^2/2R^2)} - e^{-R\Delta \sqrt{1 - \nu^2/R^2}}\right).$$
provided $R\Delta \gg 1$. Exactly the same procedure applied to Eq. (28) leads to similar result. Inserting the result Eq. (41) into Eq. (27) cancels the oscillating term $e^{i\Delta \nu}$. Therefore, the stochastic phase in the limit of fast modulation reduces to $\exp\left(-\frac{\Delta \nu^2}{2R}\right)$. It is easy to show, that Eq. (38) is valid as well for the Gaussian process $\nu \gg R^1$. The result Eqs. (38) obtained in this section for the telegraph noise modulation reduces to $\exp\left(-\frac{\Delta \nu^2}{2R}\right)$. It is easy to show, that Eq. (38) is valid as well for the Gaussian process $\nu \gg R$.

VII. SUMMARY

Theoretical investigation of the new field of single molecule non-linear spectroscopy was presented. We have obtained analytically the exact expressions for photon statistics emerging from the interaction of the pump-probe set up with a single two level system in terms of quantum trajectories. The theory clearly emphasized two types of terms: the coherent and the semiclassical, the later independent on the phase accumulated by the coherences during the delay interval between the pulses.

The following conclusions were made:

1. Unlike the line-shape in continuous wave experiments, the photon statistics obtained from pump-probe set up depends not only on the spectral shifts $\nu$, but also on the rate $R$ of the spectral diffusion process and exhibits oscillations not found in a line-shape.

2. In the limit of the impulsive pulses the spectral selectivity is lost. The information on the spectral diffusion parameters, contained only in the phase accumulated during the delay interval, is then equivalent to the information gained from a line-shape in continuous wave spectroscopy. In optics using pump-probe technique this information is expected to be difficult to detect, because of the huge bare optical frequency $\omega_0$ and dephasing effects. It will be interesting to investigate the coherence effect in multilevel systems.

3. In contrast, in the selective limit, where the laser field is weak compared to the deviations of the spectral shifts, the photon statistics offers full information on spectral diffusion parameters.

4. We have shown, that the limitation of the measurement of stochastic dynamics is determined by the conditions $RT \ll 1$ and $\Omega T \sim 1$, restricting the effectiveness of pump-probe set up only to slow processes $\nu \gg R$. Hence, to get better results our method must be improved by removing these conditions. In particular, we plan to investigate photon statistics for processes with $RT \sim 1$. In addition, our techniques can be easily modified for the investigation of relaxation processes [1], where the frequency shift may be large, thus allowing the measurement of dynamics up to the order of pico-seconds.

5. Finally, in the fast modulation limit where the stochastic transitions rate $R$ is much larger then spectral shifts $\nu$, the influence of the underlying spectral diffusion dynamics on the photon statistics reduces to the well-known Kubo-Anderson correlation function coefficient $\exp\left(-\frac{\Delta \nu^2}{2R}\right)$, which damps the contribution of the coherent terms.

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VIII. APPENDIX A

Photon Statistics. Starting with [22, 23] an interpretation of the optical Bloch formalism yields a tool for the calculation of photon statistics. The formal solution to Eq. (11) may be given by the infinite iterative expansion in $\Gamma$ [10]:

$$\sigma(t) = G(t, 0)\sigma(0) + \int_0^t dt_1 G(t, t_1)\hat{\Gamma} G(t_1, 0)\sigma(0) + \int_0^t dt_1 \int_0^{t_2} dt_2 G(t, t_2)\hat{\Gamma} G(t_2, t_1)\hat{\Gamma} G(t_1, 0)\sigma(0) + \cdots, \quad (42)$$

where $\sigma(0)$ is the initial condition, and the Green function describing the evolution of the system in the absence of spontaneous transitions into the ground state (i.e. without $\hat{\Gamma}$) is

$$G(t, t') = \hat{T} \exp \left( \int_{t'}^t L(t_1)dt_1 \right), \quad (43)$$

where $\hat{T}$ is the time ordering operator.

Each term in the expansion Eq. (42) describes the propagation of the system emitting exact number of photons: for example the first term does not include $\hat{\Gamma}$ at all, and describes a process where no photons are emitted, the second term corresponds to the processes where only one photon is emitted and so on. Therefore, $\sigma(t)$ defined as:

$$\sigma(t) = \sigma_{(t)}(0)$$

where $\sigma(t)$ describes the evolution of the system in the absence of spontaneous transitions into the ground state (i.e. without $\hat{\Gamma}$) is

$$G(t, t') = \hat{T} \exp \left( \int_{t'}^t L(t_1)dt_1 \right), \quad (43)$$

where $\hat{T}$ is the time ordering operator.
describes the conditional state of the system at the moment \(t\), provided that \(n\) photon emission events occurred in the time interval \((0, t)\), and

\[
U_{(t, t')}^{(n)} = \int_t^{t'} dt_n \cdots \int_t^{t_1} dt_1 \mathcal{G}(t, t_n) \hat{\Gamma} \cdots \hat{\Gamma} \mathcal{G}(t_1, t')
\]  

is called the \(n\)-photon-propagator.

The main equation for calculating the probability of \(n\) emission events up to time \(t\) is:

\[
P_n(t) = \langle \langle e \rangle + \langle g \rangle \rangle_{(t, 0)}^{(n)} = \langle \langle e \rangle + \langle g \rangle \rangle_{(t, 0)}^{(n)} \langle \langle \sigma(0) \rangle \rangle,
\]

which is simply the trace of the density matrix conditioned by \(n\) emission events. We showed in [22] that in the case of two separated pulses the total \(n\)-photon-propagator acting from \(t = 0\) up to \(t\) may be written as:

\[
U_{(t, t)}^{(n)} = U_{(t, t_3)}^{(n-\alpha-\beta-\gamma)} U_{(t_3, t_2)}^{(\gamma)} U_{(t_2, t_1)}^{(\beta)} U_{(t_1, 0)}^{(\alpha)},
\]

where the superscripts \(\alpha, \beta\) and \(\gamma\) are all non-negative integers leading to \(n\) emission events (i.e. \(n-\alpha-\beta-\gamma \geq 0\)).

The Einstein’s summation rule from \(0\) to \(n\) must be applied to every superscript appearing twice. Eq. (47) means that the \(n\)-photon-propagator acting in \((0, t)\) can be decomposed into the sum of all possible products of the \(\alpha\)-photon-propagator acting in \((0, t_1)\), \(\beta\)-photon-propagator acting in \((t_1, t_2)\), \(\gamma\)-photon-propagator acting in \((t_2, t_3)\) and \((n-\alpha-\beta-\gamma)\)-photon-propagator acting in \((t_3, t)\).

The propagators acting during the delay interval and after the second pulse, where the laser is off and \(\Omega = 0\), may be found immediately:

\[
U_{(t_1+\Delta, t_1)}^{(0)} = \begin{pmatrix}
e^{-\Gamma\Delta} & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & e^{i\omega_0\Delta - \frac{\Gamma}{2} \Delta} & 0 \\
0 & 0 & 0 & e^{-(i\omega_0\Delta + \frac{\Gamma}{2} \Delta)}
\end{pmatrix},
\]

\[
U_{(t_1+\Delta, t_1)}^{(1)} = \begin{pmatrix}0 & 0 & 0 & 0 \\
1 - e^{-\Gamma\Delta} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]

and

\[
U_{(t_1+\Delta, t_1)}^{(n)} = 0 \quad \text{for } n > 1.
\]

The propagators acting in \((t_3, t)\), where \(t \to \infty\), are given by the limit \(\Delta \to \infty\).

To obtain photon statistics for short pulses in the summation Eq. (47) we pick up only those processes, where the propagators acting during the pulse events are the zero-photon-propagators, i.e. \(U_{(t_1, 0)}^{(0)} = \mathcal{G}[\omega(t_1)]\) and \(U_{(t_3, t_2)}^{(0)} = \mathcal{G}[\omega(t_2)]\). We substitute Eqs. (47) into Eq. (40), and inserting the closure relation \(\sum_{j=e,g,c,c^*} |j\rangle \langle j| = 1\) between each two propagators obtain Eq. (7) of the article.

The calculation of the matrix elements \(\mathcal{G}[\omega(t)]\) is made using RWA. Applying RWA to the optical Bloch equation [11] consists of neglecting fast oscillating non-resonant terms [24]. As a result the following equation is obtained:

\[
\tilde{\sigma} = L^\text{RWA}(t) \sigma + \tilde{\Gamma} \sigma^\text{RWA},
\]

where

\[
L^\text{RWA}(t) = \begin{pmatrix} -\Gamma & 0 & -i\Omega & i\Omega \\
0 & 0 & 0 & -i\Omega \\
i\Omega & 0 & -\Gamma - i\delta(t) & 0 \\
-i\Omega & 0 & -\frac{\Gamma}{2} + i\delta(t) & 0
\end{pmatrix},
\]

and \(\delta(t)\) Eq. (11) is the detuning at moment \(t\). As discussed in the article, the detuning is assumed to be constant during the pulse. Hence, in the new representation the calculation of the Green function is simple:

\[
\mathcal{G}[\omega(t)] = \exp \left[ T L^\text{RWA}[\omega(t)] \right].
\]

Since the interaction time goes to zero \(\Gamma T \to 0\), the spontaneous emission effects during the pulses are completely suppressed, and we find:

\[
\langle \langle e | \mathcal{G}[\omega(t)] | g \rangle \rangle = (g | \mathcal{G}[\omega(t)] | e) = 1 - (g | \mathcal{G}[\omega(t)] | g) = 1 - (e | \mathcal{G}[\omega(t)] | e) = \frac{\Omega^2 \sin^2 \left( \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L - \delta w(t_j))^2}{\Omega^2}} \right)}{(\delta_L - \delta w(t_j))^2 + \Omega^2}
\]

\[
\langle \langle c \mathcal{G}[\omega(t)] c \rangle \rangle = (c^* \mathcal{G}[\omega(t)] c)^* = (g | \mathcal{G}[\omega(t)] | c) = (g | \mathcal{G}[\omega(t)] | c)^* = - (e | \mathcal{G}[\omega(t)] | e) = - (e \mathcal{G}[\omega(t)] e)^* = - (c | \mathcal{G}[\omega(t)] | c) = - (c | \mathcal{G}[\omega(t)] | c)^* =
\]
Semiclassical approximation for the two state Kubo-Anderson process.

For pulses satisfying $\frac{\delta_L-\delta w(t_j)}{\Omega} \ll 1$, i.e. resonant or impulsive pulses, from Eq. (54) we find:

$$G[\omega(t_i)] = \begin{pmatrix}
\cos^2 \frac{\Omega T}{2} & \sin^2 \frac{\Omega T}{2} & -i \sin \frac{\Omega T}{2} & i \sin \frac{\Omega T}{2} \\
\sin^2 \frac{\Omega T}{2} & \cos^2 \frac{\Omega T}{2} & i \sin \frac{\Omega T}{2} & -i \sin \frac{\Omega T}{2} \\
-i \sin \frac{\Omega T}{2} & i \sin \frac{\Omega T}{2} & \cos^2 \frac{\Omega T}{2} & \sin^2 \frac{\Omega T}{2} \\
i \sin \frac{\Omega T}{2} & -i \sin \frac{\Omega T}{2} & \sin^2 \frac{\Omega T}{2} & \cos^2 \frac{\Omega T}{2}
\end{pmatrix}. \tag{55}
$$

Substituting $\Omega T = \pi$ into Eq. (55) we see that the off-diagonal terms giving rise to coherent terms vanish. More detailed discussion on RWA and its application to the calculation of the matrix element may be found in [29].

IX. APPENDIX B

Semiclassical approximation for the two state Kubo-Anderson process. Here we present the exact expressions for $\langle P_{\text{Cl}}^n \rangle$ (n=0,1,2) for the case of the two state Kubo-Anderson process. Using Eqs. (20), Table 1, the matrix elements Eqs. (54) and Eq. (13) we find:

$$\langle P_{\text{Cl}}^1 \rangle = \frac{1 + e^{-2R\Delta}}{2} \left\{ \Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right] \times \frac{(\delta_L-\nu)^2 + \Omega^2}{(\delta_L-\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{(1-e^{-2R\Delta})}{2} \left\{ \Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right] \times \frac{(\delta_L-\nu)^2 + \Omega^2}{(\delta_L-\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{(1-e^{-2R\Delta})}{2} \left\{ \Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right] \times \frac{(\delta_L-\nu)^2 + \Omega^2}{(\delta_L-\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{\Omega^4 \sin^4 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right]}{(\delta_L-\nu)^2 + \Omega^2} + \frac{\Omega^4 \sin^4 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \right\}. \tag{56}
$$

$$\langle P_{\text{Cl}}^2 \rangle = \frac{(1+e^{-2R\Delta})(1-e^{-\Gamma\Delta})}{4} \left\{ \Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right] \times \frac{(\delta_L-\nu)^2 + \Omega^2}{(\delta_L-\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{(1-e^{-2R\Delta})(1-e^{-\Gamma\Delta})}{2} \left\{ \Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right] \times \frac{(\delta_L-\nu)^2 + \Omega^2}{(\delta_L-\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{(1-e^{-2R\Delta})(1-e^{-\Gamma\Delta})}{2} \left\{ \Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right] \times \frac{(\delta_L-\nu)^2 + \Omega^2}{(\delta_L-\nu)^2 + \Omega^2} \right. + \frac{\Omega^2 \sin^2 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \times \frac{(\delta_L+\nu)^2 + \Omega^2}{(\delta_L+\nu)^2 + \Omega^2} \right. + \frac{\Omega^4 \sin^4 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L-\nu)^2}{\Omega^2}} \right]}{(\delta_L-\nu)^2 + \Omega^2} + \frac{\Omega^4 \sin^4 \left[ \frac{\Omega T}{2} \sqrt{1 + \frac{(\delta_L+\nu)^2}{\Omega^2}} \right]}{(\delta_L+\nu)^2 + \Omega^2} \right\}. \tag{57}
$$

and

$$\langle P_{\text{Cl}}^0 \rangle = 1 - \langle P_{\text{Cl}}^1 \rangle - \langle P_{\text{Cl}}^2 \rangle. \tag{58}$$
The only approximation made in the semiclassical Eqs. is neglecting the spontaneous emission effects during the pulse events and applying RWA within the calculation of the matrix elements. Since these expressions involve the both $\nu$ and $R$, they may be used for the determination of the spectral shifts and rates.

X. APPENDIX C

Derivation of $\hat{h}[\omega(t_1),\omega(t_2),-2i\nu]$.

The two-state Kubo-Anderson process has been investigated extensively by many authors, in particular different techniques for calculation of the occupation times were proposed. Here we follow the method used in [29]. Providing the molecule was in the + state in the beginning of the first pulse and in the − state in the beginning of the second, so that exactly $m = 2k + 1$ where $k = 0, 1, 2 \cdots$ jumps occurred, it is possible to show [29], that the double Laplace transform of $\hat{m}$ in the + state in the beginning of the first pulse, and in the − state in the beginning of the second, is due to the probability to find the times between the subsequent jumps. The factor 2 in the nominator of Eq. (59) is due to the double Laplace transform of $f_{m,\Delta}(T^+)$, the PDF of the occupation time in the upper state $T^+$ for a fixed $\Delta$, is given by:

$$f_{m=0,\Delta}(u) = \hat{\chi}^k(s + u) \hat{\chi}(s) \frac{1 - \hat{\chi}(s)}{2s}, \quad (59)$$

where

$$\hat{\chi}(s + u) = \int_0^\infty e^{-\tau(s + u)} \chi(\tau) d\tau, \quad \hat{\chi}(u) = \int_0^\infty e^{-\tau u} \chi(\tau) d\tau$$

are Laplace transforms of $\chi(\tau)$ - the PDF of the waiting times between the subsequent jumps. The factor 2 in the nominator of Eq. (59) is due to the probability to find the molecule in the + state in the beginning of the first pulse, which is equal $\frac{1}{2}$ because there is symmetry between the states and we assumed stationary process. Summing up $k$ from 0 to $\infty$ we have:

$$h_s[+,-,u] = \frac{1 - \hat{\chi}(s)}{s} \frac{\hat{\chi}(s + u)}{1 - \hat{\chi}(s + u)} \hat{\chi}(s), \quad (61)$$

where $\hat{h}_s(\pm,-,u)$ is the double Laplace transform of the PDF of the occupation time in the + state, providing the system was in + state in the beginning of the first pulse and in the − state in the beginning of the second independently of the number of jumps.

Now applying Eq. (61) to the Poissonian process:

$$\chi(\tau) = Re^{-R\tau}$$

which corresponds to the correlation function $\psi(\tau)$ given by Eq. (5), and substituting $u = -2i\nu$ we find:

$$\hat{h}_s[+,-,u] = \frac{R}{2s(2R + s) - 4i(R + s)\nu}$$

Finally the inverse Laplace transform $s \rightarrow \Delta$ leads to Eq. (28) of the article:

$$\hat{h}[+,-,-2i\nu] = e^{-\Delta(R-i\nu)} \frac{\sin \left[ \Delta\sqrt{R^2 - \nu^2} \right]}{2\sqrt{R^2 - \nu^2}} \frac{R}{\nu}$$

Due to the symmetry of the stochastic process $\hat{h}[+,-,-2i\nu] = \hat{h}[+,-,2i\nu]$. The procedure of derivation of Eq. (28) for $\hat{h}[\pm,\pm,-2i\nu]$ is similar.

Note, the marginal probabilities $P[\omega(t_1),\omega(t_2)]$ of finding the molecule in state $\omega(t_1) = \pm$ during the first pulse and in state $\omega(t_2) = \pm$ during the second pulse, independently of the values of occupation times, are easy to derive from Eqs. (28) by setting $\nu = 0$ which is equal to integrating out the $T^+$ from $\hat{h}[\omega(t_1),\omega(t_2), T^+]$. Thus, the following obvious expressions are obtained:

$$P[\pm,\pm] = \frac{1 + \exp(-2R\Delta)}{4}$$

and

$$P[\pm,\mp] = \frac{1 - \exp(-2R\Delta)}{4}.$$
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[26] Originally, the contribution of the semiclassical paths to the probability of one photon emission is:
\[ P_{1}^{\text{Cl}} = \langle g | G[\omega(t_2)] | g \rangle \langle e | G[\omega(t_1)] | g \rangle \left( 1 - e^{-\Gamma \Delta} \right) + \langle e | G[\omega(t_2)] | e \rangle \langle e | G[\omega(t_1)] | g \rangle e^{-\Gamma \Delta}. \]
However, due to the symmetry of the matrix elements Eqs. [25] the trajectories multiplied by \( e^{-\Gamma \Delta} \) cancel each other.

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