Photon coincidence counting in parametric down-conversion: Interference of field-matter quantum pathways

Konstantin E. Dorfman* and Shaul Mukamel
University of California, Irvine, California 92697-2025, USA
(Received 4 April 2012; published 3 August 2012)

The coincidence rate in two detectors that register signal and idler photons in parametric down-conversion is calculated using a quantum description of the radiation field that extends the semiclassical theory to the resonance regime. The signal is given by a sum over paths in the joint field plus matter space, each involving a pair of sites (molecules) and six radiation field modes. It may not be factorized into amplitudes representing one-site, three-mode paths. All effects of multiple vacuum modes are accounted for by these paths without adding a Langevin noise source. The molecular information is given by a time-ordered superoperator Green’s function rather than the susceptibility \( \chi^{(2)} \) used in the semiclassical theory.

DOI: 10.1103/PhysRevA.86.023805
PACS number(s): 42.65.Lm, 33.80.–b, 42.50.Ar, 42.65.An

I. INTRODUCTION

The generation and manipulation of entangled light is of fundamental interest in quantum science, quantum computation, and engineering. Nearly a century after the celebrated EPR paradox [1], there remain a number of open questions regarding the creation of entangled light. Parametric down-conversion (PDC) [2,3] is an important source of entangled photons that found numerous practical applications such as quantum information technology [4,5], metrology [6], and lithography [7–9].

The standard calculation of PDC assumes that all relevant field frequencies are off resonant with matter. It is then possible to adiabatically eliminate all matter degrees of freedom and describe the process by an effective Hamiltonian for the field that contains a nonlinear cubic coupling of the modes. All matter information is embedded into a coefficient that is proportional to \( \chi^{(2)} \) [12] that is defined by the semiclassical theory of radiation-matter coupling. Langevin quantum noise is added to represent vacuum fluctuations caused by other field modes [13–15] in order to account for photon statistics.

We present a microscopic theory of type I PDC that addresses entanglement generation in a transparent way. First, it holds both on and off resonance. The resonant case is especially important for potential spectroscopic applications [16], where unique information about entangled matter [17] can be revealed. Second, it properly takes into account the quantum nature of the generated modes through a generalized susceptibility that has a very different behavior near resonance than the semiclassical \( \chi^{(2)} \). \( \chi^{(2)} \) is derived for two classical fields and a single quantum field. While this is true for the reverse process (sum frequency generation) it does not apply for PDC, which couples a single classical and two quantum modes. Third, macroscopic propagation effects are not required for the basic generation of the signal. Fourth, we include gated detection [18] that yields the finite temporal and spectral resolution of the coincident photons limited by a Wigner spectrogram. For purely time- or frequency-resolved measurement of the generated field, the signal can be expressed as a modulus square of the transition amplitude that depends on three field modes. This is not the case for photon counting.

The nature of entangled light can be revealed by photon correlation measurements that are governed by energy, momentum, and/or angular momentum conservation. In PDC, a nonlinear medium is pumped by electromagnetic field of frequency \( \omega_p \) and some of the pump photons are converted into pairs of (signal and idler) photons with frequencies \( \omega_s \) and \( \omega_i \), respectively [see Fig. 1(a)] satisfying \( \omega_p = \omega_s + \omega_i \).

In the semiclassical approach the process is described by an effective interaction Hamiltonian for the field modes

\[
H_{\text{int}}(t) = i\hbar \sum_j \int \frac{d\omega_s}{2\pi} \frac{d\omega_i}{2\pi} \frac{d\omega_p}{2\pi} \chi^{(2)}_{s,+,-}(\omega_s, \omega_i, \omega_p) \times [\hat{a}^{(s)}(\omega_s) \hat{a}^{(i)}(\omega_i) e^{i(\omega_p t - \omega_s t - \omega_i t)} + \text{H.c.}],
\]

where \( \hat{a}^{(s)} \) and \( \hat{a}^{(i)} \) are creation operators for signal and idler modes, \( \chi^{(2)} \) is the expectation value of the classical pump field, \( \Delta k = k_p - k_i - k_s \). \( j \) runs over molecules, and \( \chi^{(2)}_{s,+,-} \) [normally denoted \( \chi^{(2)}(-i\omega_s, -i\omega_i, i\omega_p) \)] is the second-order nonlinear susceptibility [the reason for the new notation will be clarified below]

\[
\chi^{(2)}_{s,+,-}(\omega_s, \omega_i, \omega_p) = \left( \frac{i}{\hbar} \right)^2 \int_0^\infty dt_2 \int_0^\infty dt_1 e^{i(\omega_0 t_2 + t_1)} \chi^{(2)}(\omega_0, \omega_s, \omega_i, \omega_p) \times \left[ \frac{1}{2} (V(t_2, t_1), V(0, t_1)) + (i \leftrightarrow p) \right].
\]

We have introduced superoperator notation that provides a convenient bookkeeping of time-ordered Green’s functions. With every ordinary operator \( A \) we associate two superoperators defined by their action on an ordinary operator \( X \) as \( A_L = AX \) acting from left and \( A_R =XA \) (right). We further define the symmetric and antisymmetric combinations \( A_s = \frac{1}{2}(A_L + A_R) \) and \( A_a = \frac{1}{2}(A_L - A_R) \). Thus, the “\( + - \)” indices in Eq. (2) signify two commutators followed by an anticommutator. The bottom line of the semiclassical approach is that PDC is represented by three-point matter-field interaction via the second-order susceptibility \( \chi^{(2)}_{s,+,-} \) that

*kdorfman@uci.edu

1050-2947/2012/86(2)/023805(8) 023805-1 ©2012 American Physical Society
couples the signal, idler, and pump modes. However, it has been realized, that other field modes are needed to yield the correct photon statistics. Electromagnetic field fluctuations are then added as quantum noise (Langevin forces) [13].

II. MICROSCOPIC SUPEROPERATOR APPROACH TO PDC

Here we present a fully microscopic calculation of the coincidence count rate in type I PDC [19]. We show that PDC is governed by a quantity that resembles but is different from (2). In contrast with the semiclassical approach, PDC emerges as a six-mode two-molecule rather than a three-mode matter-field interaction process and is given by convolution of two quantum susceptibilities \( \chi_{LL}^{(2)}(\omega_s,\omega_i,\omega_p) \) and \( \chi_{LL}^{(2)}(\omega_s',\omega_i',\omega_p') \) that represent a pair of molecules in the sample interacting with many vacuum modes of the signal (\( s, s' \)) and the idler (\( i, i' \)). Field fluctuations are included self-consistently at the microscopic level. Furthermore, the relevant nonlinear susceptibility is different from the semiclassical one \( \chi_{LL}^{(2)}(\omega_s,\omega_i,\omega_p) \) and is given by

\[
\chi_{LL}^{(2)}(\omega_s,\omega_i,\omega_p) = \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_1 e^{i(\omega_s t_2 + \omega_i t_1) + i\omega_p t_1} \times \langle [V(t_2 + t_1)V(t_1),V(0)] \rangle + (i \leftrightarrow s). \tag{3}
\]

Equation (3) has a single commutator and is symmetric to a permutation of \( \omega_i \) and \( \omega_p = \omega_s - \omega_i \), as should. Equation (2) has two commutators and lacks this symmetry.

Our calculation of the coincidence rate of signal and idler photons starts with the definition [14]

\[
R_e(\tilde{\omega}_s,\tilde{\omega}_i;\tilde{\omega}_s',\tilde{\omega}_i') = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \langle E_{ij}^{(i)}(t_i)E_{ij}^{(i')}(t_i')E_{ij}^{(s)}(t_s)E_{ij}^{(s')}\rangle, \tag{4}
\]

where the angular brackets in the correlation function denote \( \cdots \equiv \text{tr}(\cdots \rho) \) where \( \rho \) is the field plus matter density operator. Here \( E_{ij}^{(s)} \) is the time-and-frequency-gated electric field measured by detector, which will be clarified in Sec. II B. The gate is characterized by mean frequency \( \tilde{\omega}_s \) and time \( t_s \), (\( v = s,i \)).

A. Bare coincidence rate

We first calculate the “bare” correlation function [18] (no gating) \( \langle E_{ij}^{(i)}(t_i')E_{ij}^{(s)}(t_s)E_{ij}^{(s')} \rangle \) which represents four spectral modes arriving at the detectors, where modes \( s, s', i, \) and \( i' \) are defined by their frequencies \( \omega_s, \omega_i, \omega_p = \omega_s - \omega_i, \) and \( \omega_s' = \omega_p - \omega_i' \). This is given by a time ordered product of Green’s functions of superoperators in the interaction picture

\[
\langle [T E_{ij}^{(i)}(t_i')E_{ij}^{(s)}(t_s + t_i)E_{ij}^{(s')}E_{ij}^{(i)}(t_i - t_i')] \times e^{-(i/h)\int_{-\infty}^t \sum_{\nu} \gamma_{\nu}^{(i)}(t') \rho(\infty)} \rangle. \tag{5}
\]

The radiation-matter coupling superoperator is

\[
V'(t) = \sum_{s,i,p} \left[ E_{ij}^{(i)}(t) V_L(t) - E_{ij}^{(i)}(t) V_R(t) \right] + \text{H.c.} \tag{6}
\]

\( V'(t) \) is a matter raising (lowering) operator so that \( V_L(t) = \mu_{ij} |g\rangle\langle f| e^{-i(\omega_{ij} t + \gamma_{ij} t^2)} + \mu_{eg} |g\rangle\langle f| e^{-i(\omega_{eg} t + \gamma_{eg} t^2)} + \mu_{ef} |f\rangle\langle e| e^{-i(\omega_{ef} t + \gamma_{ef} t^2)}, \) where \( \mu_{ij}, \gamma_{ij}, \gamma_{ij} \) and \( \omega_{ij} \) are the corresponding dipole moment, linewidth, and transition frequency of the transition \( i \leftrightarrow j, (i = g,e,f). \)

In type I PDC the sample is composed of \( N \) identical molecules initially in their ground state. They interact with one classical pump mode and emit two spontaneously generated quantum modes with the same polarization into two collinear cones. The initial state of the optical field is given by \( |0\rangle, 0 \rangle, |\beta\rangle \) and \( |g\rangle \) is the classical pump field. This pump field promotes the molecule from its ground state \( |g\rangle \) to the doubly excited state \( |f\rangle \) [see Fig. 1(b)].

Due to the quantum nature of the signal and the idler fields, the interaction of each of these fields with matter must be at least second order to yield a nonvanishing trace in Eq. (5). Therefore, the perturbative expansion of the integral in the exponent of Eq. (5) will contain ten field-matter interactions: six with the sample molecules (two with each of the signal, idler, and pump fields) and the last four are with the detectors. Note that there can be no interactions during the intervals \( t_s \) and \( t_i \). In that case the field correlation function will vanish since \( \delta|0\rangle = 0 \). Thus, the leading contribution to Eq. (5) comes from the four diagrams shown in Fig. 2 (for rules see [19]).

The coherent part of the signal represented by the interaction of two spontaneously generated quantum modes and one classical mode is proportional to the number of pairs of sites in the sample \( \sim N(N - 1) \), which dominates the other, incoherent, \( \sim N \) response for large \( N \). Details of the calculation of the correlation function (5) are presented in the Appendix. We obtain for the bare coincidence rate

\[
R_e^{(s)}(\omega_s,\omega_i',\omega_p,\omega_i) = N(N - 1) \left( \frac{2\pi R^4}{V} \right)^4 E^{(s)}(\omega_s') E^{(p)}(\omega_p') D(\omega_s - \omega_i') \times D(\omega_p') D(\omega_p - \omega_i') \chi_{LL}^{(2)}[\omega_s - \omega_i', - \omega_i', \omega_i'],
\]

where \( E^{(p)}(\omega) \equiv E^{(p)}(\omega) b^{(p)}(\omega) \) is a classical field amplitude, \( E^{(p)}(\omega) \) is the pump pulse envelope, and \( D(\omega) = \omega D(\omega), \)
where $\bar{D}(\omega) = \sqrt{\omega^3/\pi^2}c^3$ is the density of radiation modes. For our level scheme [Fig. 1(b)] the nonlinear susceptibility

$$
\chi_{LL}^{(2)}[\omega_p, -\omega_i, \omega'_p, \omega'_i] = \frac{1}{\hbar}\langle g' | T V_L G(\omega'_p - \omega'_i) V_L G(\omega'_p | V_L^\dagger g' \rangle + \frac{1}{\hbar}\langle g' | T V_L G(\omega'_p - \omega'_i) V_L G(\omega'_p | V_L^\dagger g' \rangle
$$

where $G(\omega) = 1/(\omega - H_0/\hbar + i\gamma)$ is the retarded Liouville Green’s function, and $\gamma$ is lifetime broadening. $\chi_{LL}^{(2)}$ possesses a permutation symmetry with respect to $s \leftrightarrow t$ (both have $L$ index). In contrast the semiclassical calculation via $\chi^{(2)}_{+-}$ is nonsymmetric with respect to $s \leftrightarrow i$(one + and one − indexes), which results in a coincidence count rate that depends upon whether the signal or idler detector clicks first [20].

**B. Detected coincidence rate**

We shall calculate the coincidence rate registered by two detectors, $D_s$ and $D_i$, whose inputs are located at $t_s^{(i)}$ for a signal and at $r_s^{(i)}$ for an idler. Both detectors consist of a time gate $T^{(i)}$ centered at $t_s$ followed by a frequency gate $T^{(i)}_f$ centered at $\omega_s$, where $x = s, i$ indicates signal or idler. First, the time gate transforms the electric field of the mode $x$ given by $E^{(x)}(t) = \sum_j E_j^{(x)}(\tau_{j}^{(x)}, t)$ with $E_j^{(x)}(\tau_{j}^{(x)}, t) = E_j^{(x)}(r_s^{(x)}, \omega_s) e^{-i\omega_s t}$ as follows:

$$
E_j^{(x)}(t) = F_j^{(s)}(t, \tau_{j}^{(x)}) E_j^{(x)}(r_s^{(x)}, t).
$$

Thus the count rate $R_s$ for the signal is given by

$$
R_s = \sum_j |F_j^{(s)}(t_{j}^{(s)}, \tau_{j}^{(x)})|^2 E^{(s)}(r_s^{(s)}, \omega_s)^2 e^{-i\omega_s t_{j}^{(s)}} dt_{j}^{(s)}.
$$

FIG. 3. (Color online) Loop diagrams for the interaction of three classical pump, signal, and idler fields. Left and right loop diagrams correspond to the first and second terms in Eq. (9), respectively. Each loop has two possible permutations of $i/s$ corresponding to the time ordering between idler and signal photons.

FIG. 2. (Color online) Loop diagrams for the coincidence count rate of signal and idler photons generated in type I PDC [Eq. (5)]. The left and right diagrams represent a pair of molecules. Curvy blue (straight red) arrows represent field-matter interaction with the sample (detectors). There are four possible permutations ($s/i$ and $i/s$). This leads to four terms when Eq. (8) is substituted into Eq. (7).

Equation (7) represents a six-mode ($\omega_p, \omega_i, \omega_q, \omega'_p, \omega'_i, \omega'_q$) field-matter correlation function factorized into two generalized susceptibilities, each representing the interaction of two quantum and one classical mode with a different molecule. Because of the two constraints $\omega_p = \omega_i + \omega_q$ and $\omega'_p = \omega'_i + \omega'_q$ that originate from time translation invariance on each of the two molecules that generate the nonlinear response, Eq. (7) only depends on four field modes. Each molecule creates a coherence in the field between states with zero and one photon. By combining the susceptibilities from a pair of molecules we obtain a photon occupation number that can be detected. Thus, the detection process must be described in the joint space of the two molecules and involves the interference of four quantum pathways (two with bra and two with ket) with different time orderings. Note that this pathway information is not explicit in the Landevign approach.

For comparison, if all three fields (signal, idler, and pump) are classical, the number of material-field interactions is reduced to three—one for each field. Then the leading contribution to the field correlation function shown in Fig. 3 yields the semiclassical nonlinear susceptibility $\chi^{(2)}_{+-}$.
Then, the frequency gate is applied, \( E^{(s)}_{\text{f}}(r_G^{(s)}, \omega) = F_f(\omega; \omega_s) E^{(s)}_{\text{f}}(r_G^{(s)}, \omega) \), where \( E^{(s)}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} E^{(s)}(t) \). We thus obtain the time-and-frequency-gated field \( E_{\text{f}}(t) \). We assume that the time gate is applied first. Therefore, the combined detected field at the position \( r_D \) can be written as
\[
E^{(s)}_{\text{f}}(r_D^{(s)}, t) = \int_{-\infty}^{\infty} dt' F^{(s)}(t - t', \omega_s) F^{(s)}(t', \omega_s) E^{(s)}(t') (t' - t),
\]
where \( E^{(s)}(\omega) = \sum_{\omega_s, \omega} \sqrt{2\pi} \delta(\omega - \omega_s) V \hat{a}_s e^{-i\omega t} \) (\( V \) is a mode quantization volume). For simplicity we omit the position dependence in the fields and assume that propagation between \( r_G^{(s)} \) and \( r_D^{(s)} \) is included in the spectral gate function.

The measured coincidence rate of photons coming from signal and idler fields is given by Eq. (4). In order to provide a clean bookkeeping for all interactions we describe the bare signal in terms of Liouville space “left” and “right” superoperators \( 18 \)

\[
W^{(s)}(\omega_s^l, \omega_i^l; \omega_s^r, \omega_i^r) = W^{(s)}(\omega_s^l, t_s^l, \omega_s^r, t_s^r) W^{(i)}(\omega_i^l, t_i^l, \omega_i^r, t_i^r),
\]
where
\[
W^{(s)}(\omega_s^l, t_s^l, \omega_s^r, t_s^r) = \int_{-\infty}^{\infty} d\omega_s \left[ F_s^{(s)}(\omega_s^l, \omega_s^r) \right]^2 e^{-i\omega_s (t_s^l - t_s^r)},
\]
and
\[
W^{(i)}(\omega_i^l, t_i^l, \omega_i^r, t_i^r) = \int_{-\infty}^{\infty} d\omega_i \left[ F_i^{(i)}(\omega_i^l, \omega_i^r) \right]^2 e^{-i\omega_i (t_i^l - t_i^r)}.
\]

Taking into account Eq. (A18) we redefine the bare signal according to Eq. (7). We further modify the gating spectrogram that controls the temporal and spectral resolution of the

\[
W^{(s)}(\Delta \omega_s; \Delta t_s) = \int_{-\infty}^{\infty} d\omega_s \int_{-\infty}^{\infty} dt_s e^{-i\omega_s \Delta \omega_s} e^{-i\omega_i \gamma_s \Delta t_s},
\]

where \( \omega_i = \omega_s - \omega_i \).

\[
W^{(i)}(\Delta \omega_i; \Delta t_i) = \int_{-\infty}^{\infty} d\omega_i \int_{-\infty}^{\infty} dt_i e^{-i\omega_i \Delta \omega_i} e^{-i\omega_i \gamma_i \Delta t_i},
\]

with
\[
W_s^{(s)}(t_s^l, \omega_s^r, \omega_s^l, t_s^r) = \int_{-\infty}^{\infty} d\tau_s \int_{-\infty}^{\infty} d\omega_s \int_{-\infty}^{\infty} d\omega_i \left[ F_s^{(s)}(\omega_s^l, \omega_s^r) \right]^2 e^{-i\omega_s \tau_s} F^{(s)}(t_s^l + \tau_s, \omega_s^r, \omega_s^l, t_s^r),
\]

\[
W_i^{(i)}(t_i^l, \omega_i^r, \omega_i^l, t_i^r) = \int_{-\infty}^{\infty} d\tau_i \int_{-\infty}^{\infty} d\omega_i \int_{-\infty}^{\infty} d\omega_s \left[ F_i^{(i)}(\omega_i^l, \omega_i^r) \right]^2 e^{-i\omega_i \tau_i} F^{(i)}(t_i^l + \tau_i, \omega_i^r, \omega_i^l, t_i^r).
\]
FIG. 5. (Color online) Absolute value of semiclassical susceptibility $|\chi^{(2)}_{+\to-}\rangle\langle -|\omega_p - \omega_i, -\omega_i, \omega_p|\rangle$ (arb. units) (9) (a), and quantum susceptibility $|\chi^{(2)}_{LL}\rangle\langle -|\omega_p - \omega_i, -\omega_i, \omega_p|\rangle$ (8) (b) vs pump $\omega_p$ and idler frequency $\omega_i$. We used the standard KTP parameters outlined in the text. Left column: real (c), imaginary part (e), and absolute value (g) of $\chi^{(2)}_{+\to-}$ (red line) and $\chi^{(2)}_{LL}$ (blue line) for off-resonant pump $\omega_p - \omega_{eg} = 10\gamma_{ef}$. Right column: (d), (f), and (h)—same as (c), (e), and (g) but for resonant pump $\omega_p \approx \omega_{eg}$.

the regime covered by the semiclassical theory, where the susceptibility is assumed to be a constant. Similar agreement between classical and quantum susceptibilities can be observed if the pump is resonant with two-photon transition $\omega_p \approx \omega_{eg}$ but the idler is off resonance $\omega_i \approx \omega_{eg}$ [Figs. 5(d), 5(f), and 5(h)]. However, close to resonance [Figs. 5(a) and 5(b)] the two susceptibilities are very different. The semiclassical susceptibility $\chi^{(2)}_{+\to-}$ vanishes at resonance, while the quantum susceptibility $\chi^{(2)}_{LL}$ reaches its maximum.

To put the present ideas into more practical perspective we show in Fig. 6 the coincidence count rate for a monochromatic pump $\omega_p$ and mean signal detector frequency $\tilde{\omega}_s$. The quantum theory yields one strong resonant peak at $\tilde{\omega}_s = \omega_p - \omega_{eg}$ and two weak peaks at $\omega_p = \omega_{eg}$ and $\tilde{\omega}_s = \omega_{eg}$ if the idler detector is resonant with the intermediate state $|e\rangle$; $\tilde{\omega}_s = \omega_{eg}$ [Fig. 6(a)]. However, if we tune the idler detector to a different frequency, for instance $\omega_{eg} - \tilde{\omega}_s = 2$ GHz, there is an additional peak at $\tilde{\omega}_s = \omega_p - \tilde{\omega}_s$ [Fig. 6(b)]. Similarly, when the pump consists of two monochromatic beams $\omega_p \neq \omega'_p$ [panels (c) and (d)] the number of peaks are doubled compared to a single monochromatic pump. Clearly, one can reproduce the exact same peaks for $\omega'_p$ as for $\omega_p$.

FIG. 6. (Color online) Left column: two-dimensional coincidence counting rate (log scale in arb. units) calculated using quantum theory, Eq. (19), assuming a single monochromatic pump with frequency $\omega_p$. Idler detector resonant with intermediate level $\tilde{\omega}_s = \omega_{eg} = 282$ THz (a), while $\omega_{eg} - \tilde{\omega}_s = 2$ GHz for (b). Right column: same as left but for a pump made out of two monochromatic beams with frequencies $\omega_p = \omega'_p = 2 \times 10^{-5} \omega_{eg}$.

Shwartz et al. recently reported PDC in diamond, where an 18 keV pump field generates two x-ray photons [20]. They have shown that the semiclassical calculation without Langevin noise agrees with experiment only far from degeneracy $\tilde{\omega}_s \approx \omega_p/2$ but yields a factor of 2 smaller count rate close to degenerate frequency $\tilde{\omega}_s = \omega_p/2$ and strongly depends on which detectors register the photon first. To overcome this problem they added a Langevin noise to take into account other vacuum modes. Our calculation (solid line in Fig. 7) reproduces experiment (dots) in the entire frequency range without adding noise. The noise comes from the summation over $\omega_p$, $\omega'_p$, $\tilde{\omega}_s$, and $\tilde{\omega}_p$. In simulations we assumed $\omega_{eg} = 280$ eV, $\omega_p = \omega'_p = 18$ keV, and fixed the idler detector position at $\tilde{\omega}_s = 9$ keV, which corresponds to an off-resonant parameter regime. Therefore, the result is independent of the frequency variations of the susceptibility. Figure 7 rather illustrates the photon detection treated in the joined space of two sites.

FIG. 7. (Color online) Simulated coincidence count rate in Eq. (19) vs $2\tilde{\omega}_s/\omega_p$, $\tilde{\omega}_s$, and $\omega_p/2$ are the mean frequency of the signal detector and the degenerate photon frequency, respectively. Dots represent the experimental results of Shwartz et al. [20].
IV. CONCLUSIONS

In summary, a microscopic treatment of the photon counting in PDC that applied to resonant as well as off-resonant frequencies reveals that it is given by a sum over six-mode paths that involves a pair of molecules in the sample. The two constraints $\omega_0 = \omega_s + \omega_i$ and $\omega^\prime = \omega_i + \omega_s$ reduce the number of independent frequency modes to four. The correct photon statistics due to the presence of multiple signal and idler vacuum modes is reproduced. The time-and-frequency resolution of the measurement is controlled by the gate parameters.

ACKNOWLEDGMENTS

We would like to thank Professor S. E. Harris and Dr. S. Schwartz for sharing their experimental results and for their useful discussions. We gratefully acknowledge the support of the National Science Foundation through Grant No. CHE-1058791. Computations are supported by CHE-0840513, the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy.

APPENDIX: CALCULATION OF THE BARE COINCIDENCE RATE

Since initially both signal and idler modes are in the vacuum state $|0\rangle$ and the final state is $|1\rangle|1\rangle$, the interaction of each of these fields with matter that yields a nonvanishing trace must be at least second order. Therefore, the perturbative expansion of the integral in the exponent of Eq. (5) will contain ten field-matter interactions (six with the sample and four with the detectors). The number of diagrams is reduced by noting that two interactions occur with each of the pump, signal, and idler fields. Another simplification arises since there can be no two interactions during the interval $\tau_s$ and $\tau_i$, since in that case the field correlation function will vanish since $\hat{\alpha}(0) = 0$. Finally, since the signal and idler fields are initially in the vacuum state the correct combination of the fields must be $E_R^{(s)}(t)E_R^{(i)}(t')$.

The leading contribution to the field correlation function shown in Fig. 2 is thus given by the time-ordered superoperator correlation function

$$J(t_1, \ldots, t_4) = j(E_{R}^{(s)}(t_4)E_{R}^{(i)}(t_3)E_{R}^{(s)}(t_2)E_{R}^{(i)}(t_1)) \times E_{L}^{(s)}(t_4)E_{L}^{(i)}(t_3)E_{L}^{(s)}(t_2)E_{L}^{(i)}(t_1) \times E_{R}^{(p)}(t_2)E_{R}^{(p)}(t_1), \tag{A1}$$

where $t_1 = t_1' + \tau_s$, $t_2 = t_2' + \tau_i$, and $t_3 = t_3' - \tau_i$ are the interaction times with the detection. We can factorize Eq. (A1) into the product of signal, idler, and pump correlation functions, which yields

$$J(t_1, \ldots, t_4) = \langle E_R^{(s)}(t_1, t_2, t_3, t_4) \rangle \langle E_L^{(s)}(t_1, t_2, t_3, t_4) \rangle \langle E_R^{(i)}(t_1, t_2, t_3, t_4) \rangle \langle E_L^{(i)}(t_1, t_2, t_3, t_4) \rangle \langle E_R^{(p)}(t_1, t_2, t_3, t_4) \rangle \tag{A2}$$

where

$$J(t_1, \ldots, t_4) = \langle E_R^{(s)}(t_1, t_2, t_3, t_4) \rangle \langle E_L^{(s)}(t_1, t_2, t_3, t_4) \rangle \langle E_R^{(i)}(t_1, t_2, t_3, t_4) \rangle \langle E_L^{(i)}(t_1, t_2, t_3, t_4) \rangle \langle E_R^{(p)}(t_1, t_2, t_3, t_4) \rangle \tag{A3}$$

$$\langle \alpha^{(s)}(t_4) \alpha^{(i)}(t_3) \alpha^{(s)}(t_2) \alpha^{(i)}(t_1) \rangle \times \langle \alpha^{(s)}(t_1) \alpha^{(i)}(t_2) \alpha^{(s)}(t_3) \alpha^{(i)}(t_4) \rangle \times \langle \alpha^{(s)}(t_2) \alpha^{(i)}(t_3) \alpha^{(s)}(t_4) \alpha^{(i)}(t_1) \rangle \times \langle \alpha^{(s)}(t_3) \alpha^{(i)}(t_4) \alpha^{(s)}(t_1) \alpha^{(i)}(t_2) \rangle \times \langle \alpha^{(s)}(t_4) \alpha^{(i)}(t_1) \alpha^{(s)}(t_2) \alpha^{(i)}(t_3) \rangle.$$

This implies that only certain pairs of modes yield nonzero correlation functions. Taking into account that the mode frequencies are given by $\omega_0^{(s)} = \omega_s$, $\omega_0^{(i)} = \omega_i - \Omega_s$, $\omega_0^{(s)} = \omega_i + \Omega_s$, and $\omega_0^{(i)} = \omega_i$. Eq. (A3) yields

$$J(t_1, t_2, t_3, t_4) = \langle f(\omega_s) \rangle^2 \langle f(\omega_i) \rangle^2 e^{-i\omega_s(t_4-t_1)+i\omega_i(t_2-t_3)}.$$

The two-point pump correlation function is given by

$$J(t_1, t_2) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \omega_0 \omega_0' = \langle f(\omega_s) \rangle^2 \langle f(\omega_i) \rangle^2 e^{-i\omega_s(t_4-t_1)+i\omega_i(t_2-t_3)}.$$
We can now calculate the entire correlation function
\[
\left\{ T E_R^{(i)}(t_i) E_R^{(i)}(t_i + \tau_i) T E_L^{(s)}(t_s) E_L^{(s)}(t_s + \tau_s) \right\} \exp \left[ -i \int_{-\infty}^{\infty} \sqrt{2} H_{\text{int}}(\tau) \, d\tau \right] \rho(-\infty)
\]
\[
= \frac{N(N-1)}{(2\pi)^{2}} \left( \frac{-i\sqrt{2}}{\hbar} \right)^{6} \int_{-\infty}^{\infty} d\omega_p \, d\omega_p' \, f(\omega_p)^2 \frac{1}{\omega_p - \omega_p'} f(\omega_p' - \omega_s - \Omega_s) f(\omega_p + \Omega_s) f(\omega_p + \omega_p' - \omega_s - \Omega_s) f(\omega_p + \omega_p' + \Omega_s) \Xi, \quad (A12)
\]
where
\[
\Xi = \int_{-\infty}^{\infty} dt_1 dt_2 dt_3 dt_4 dt_5 dt_6 \, e^{i\omega_1 t_1 + i\Omega_1 t_1 + i\omega_2 t_2 - i\Omega_2 t_2} \delta(\omega_p - \omega_2 - \omega_p') \delta(\omega_p' - \omega_2 + \omega_p - \omega_s + \Omega_s) \delta(\omega_p + \omega_p' + \omega_s - \omega_p - \omega_s - \Omega_s) \times \langle g | T V_L^{(i)} g(t_6 - t_3) V_L^{(i)} g(t_4 - t_1) V_L^{(p)} g | t_5 - t_3 \rangle V_R^{(i)} g(t_5 - t_3) V_R^{(p)} g(t_5 - t_3) V_L^{(p)} g. \quad (A13)
\]
To evaluate \( \Xi \) we must take into account all possible time orderings of \( t_1, \ldots, t_6 \). This gives four terms \( \Xi = \Xi_a + \Xi_b + \Xi_c + \Xi_d \) represented by the loop diagrams as marked in Fig. 2:
\[
\Xi_a = \int_{-\infty}^{\infty} \delta(\omega_p - \omega_2 - \omega_p') \delta(\omega_p' - \omega_2 + \omega_p - \omega_s + \Omega_s) \delta(\omega_p + \omega_p' + \omega_s - \omega_p - \omega_s - \Omega_s) \times \langle g | T V_L^{(i)} g(t_6 - t_3) V_L^{(i)} g(t_4 - t_1) V_L^{(p)} g | t_5 - t_3 \rangle V_L^{(p)} g. \quad (A14)
\]
\[
\Xi_b = \int_{-\infty}^{\infty} \delta(\omega_p - \omega_2 - \omega_p') \delta(\omega_p' - \omega_2 + \omega_p - \omega_s + \Omega_s) \delta(\omega_p + \omega_p' + \omega_s - \omega_p - \omega_s - \Omega_s) \times \langle g | T V_L^{(i)} g(t_6 - t_3) V_L^{(i)} g(t_4 - t_1) V_L^{(p)} g | t_5 - t_3 \rangle V_L^{(p)} g. \quad (A15)
\]
\[
\Xi_c = \int_{-\infty}^{\infty} \delta(\omega_p - \omega_2 - \omega_p') \delta(\omega_p' - \omega_2 + \omega_p - \omega_s + \Omega_s) \delta(\omega_p + \omega_p' + \omega_s - \omega_p - \omega_s - \Omega_s) \times \langle g | T V_L^{(i)} g(t_6 - t_3) V_L^{(i)} g(t_4 - t_1) V_L^{(p)} g | t_5 - t_3 \rangle V_L^{(p)} g. \quad (A16)
\]
\[
\Xi_d = \int_{-\infty}^{\infty} \delta(\omega_p - \omega_2 - \omega_p') \delta(\omega_p' - \omega_2 + \omega_p - \omega_s + \Omega_s) \delta(\omega_p + \omega_p' + \omega_s - \omega_p - \omega_s - \Omega_s) \times \langle g | T V_L^{(i)} g(t_6 - t_3) V_L^{(i)} g(t_4 - t_1) V_L^{(p)} g | t_5 - t_3 \rangle V_L^{(p)} g. \quad (A17)
\]
Combining Eqs. (A14)–(A17) we can connect the signal to the nonlinear susceptibility \( \chi_{LL-}^{(2)} \):
\[
\left\{ T E_R^{(i)}(t_i) E_R^{(i)}(t_i + \tau_i) T E_L^{(s)}(t_s) E_L^{(s)}(t_s + \tau_s) \right\} \exp \left[ -i \int_{-\infty}^{\infty} \sqrt{2} H_{\text{int}}(\tau) \, d\tau \right] \rho(-\infty)
\]
\[
= \frac{N(N-1)}{(2\pi)^{2}} \left( \frac{-i\sqrt{2}}{\hbar} \right)^{6} \int_{-\infty}^{\infty} \frac{d\omega_p \, d\omega_p'}{2\pi} \delta(\omega_p - \omega_2 - \omega_p') \delta(\omega_p' - \omega_2 + \omega_p - \omega_s + \Omega_s) \delta(\omega_p + \omega_p' - \omega_s + \omega_p - \omega_p) \times \langle g | T V_L^{(i)} g(t_6 - t_3) V_L^{(i)} g(t_4 - t_1) V_L^{(p)} g | t_5 - t_3 \rangle V_L^{(p)} g. \quad (A18)
\]
where
\[
2^{-1/2} \chi_{LL-}^{(2)} \left[ -(\omega_p - \omega_p'), -\omega_2 \right] = \frac{1}{\hbar} \left( \langle g | T V_L^{(i)} g(t_6 - t_3) V_L^{(i)} g(t_4 - t_1) V_L^{(p)} g | t_5 - t_3 \rangle V_L^{(p)} g \right)
\]
\[
= \frac{1}{\hbar} \left( \frac{\mu_{ij} \mu_{ij} \mu_{ij}}{\omega_p - \omega_s} + i \gamma_{gg} \right) \left[ \omega_p + \omega_p' - \omega_s - i \gamma_{gg} \right]. \quad (A19)
\]
where \( \mu_{ij}, \gamma_{ij}, \gamma_{ij} \), and \( \omega_{ij} \) are dipole moment, linewidth, and transition frequency corresponding to a given transition \( i \leftrightarrow j \).

Note that \( \chi_{LL-}^{(2)} \) is different from the semiclassical \( \chi_{++}^{(2)} \).

Physically, this is clear, since \( \chi_{++}^{(2)} \) is symmetric with respect to permutation of \( s \leftrightarrow i \), while the classical result of \( \chi_{++}^{(2)} \) is not. \( \omega_{ij} \) is “+” and \( \omega_{ij} \) is “−”.

This can be seen by comparing (A19) and (9).

If the energies of the signal \( \omega_p \) and idler \( \omega_p' \) are far from the degenerate values \( \omega_p/2 \) and \( \omega_p'/2 \), respectively, then for \( \omega_s \gg \omega_p - \omega_s \) and \( \omega_p' \gg \omega_p - \omega_p' \), the \( \chi_{++}^{(2)} \) coincides with \( \chi_{LL-}^{(2)} \). (see Ref. [19]). Furthermore, if the signal and idler have only single-mode components, then phase matching yields \( \delta(\omega_p + \omega_p' - \omega_s) \) with \( \omega_0 = \omega_p' \) so that the result is governed by \( \chi_{LL-}^{(2)} \). (Ref. [19]).

To gain deeper physical insight we note, that Eq. (A18) is expressed as a convolution of two generalized nonlinear susceptibilities \( \chi_{LL-}^{(2)} \)-calculated in the jointed field-matter space of two molecules. This description is similar to a transition amplitude approach that is often used in homodyne detection. The field wave function
\[
|\psi\rangle = |0\rangle + \sum_{i,s} T(i,s) \hat{a}_{i}^{\dagger} \hat{a}_{s}^{\dagger} |0\rangle, \quad (A20)
\]
where the transition amplitude $T(s,i)$ is given by

$$T(s,i) = \sqrt{\frac{2\pi\hbar\omega_i}{V}} \sqrt{\frac{2\pi\hbar\omega_s}{V}} \int_{-\infty}^{\infty} \frac{d\omega_p}{2\pi} \mathcal{E}(\omega_p) \delta(\omega_i + \omega_s - \omega_p) \chi^{(2)}_{LL}[\omega_i, -\omega_s, -\omega_i, \omega_p]$$  \hspace{1cm} (A21)

can be rewritten as a sum of two terms that represent two pathways ($i$ arrives first or $s$ arrives first). The field density matrix $|\psi\rangle\langle\psi|$ has four pathways—two for the bra and two for the ket (see Fig. 2). The gating must be described by the density matrix in the joint space of two molecules and it involves the interference of all four pathways. In other words since each $\chi^{(2)}_{LL}$ depends on the signal, idler, and pump, one cannot say that the signal and idler are generated at different molecules. Rather, each molecule creates a coherence in the field between states with zero and one photon, and by combining the amplitudes from a pair of molecules we get a photon occupation number that can subsequently be further detected.