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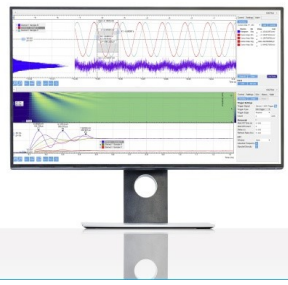

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ABSTRACT

Glauber's $g^{(2)}$-function provides a common measure of quantum field statistics through two-photon coincidence counting in Hanbury Brown–Twiss measurements. Here, we propose to use nonlinear optical signals as a tool for the characterization of quantum light. In particular, we show that Raman measurements provide an alternative direct probe for a different component of the four-point correlation function underlying the $g^{(2)}$-function. We illustrate this capacity for a specific quantum state obtained from a frequency conversion process. Our work points out how the analysis of controlled optical nonlinear processes can provide an alternative window toward the analysis of quantum light sources.

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The photon counting formalism developed by Glauber[1] lies at the very heart of quantum optics. It has been instrumental in the characterization of light—whether it is quantum fluctuations of light fields,[2] the particle nature of Fock states,[3] or the violation of Bell's inequality for photons.[4–6] On a formal level, photon correlation measurements characterize quantum fields in terms of *normally ordered* multipoint correlation functions, while photon fluctuations are described by non-normally ordered correlation functions.

The standard theory of photon counting[2] treats the detector as an ideal two-level system. As pointed out in Ref. 7, any spectroscopic measurement may be interpreted as a photon counting experiment, provided that the two-level systems are replaced by more complex quantum systems. Given the great interest in exploiting quantum correlations of light for quantum sensing or spectroscopy,[8–12] this paper extends this idea and demonstrates that nonlinear optical signals—and, in particular, Raman measurements—may also offer an avenue for the characterization of multimode quantum fields. We show, in particular, how Raman measurements can provide information about a quantum state of light, which cannot be extracted in photon counting.

A QED formulation of nonlinear optical signals depends on *time-ordered* multi-point field correlation functions of the form[13,14] $\sim \langle \mathcal{T} E_1^\dagger(\tau_1) E_2^\dagger(\tau_2) E_3(\tau_3) E_4(\tau_4) \rangle$, where $\mathcal{T}$ denotes the time-ordering operator and $E_1 \ldots E_4$ are the various light fields in the signal, which are convoluted with the sample's nonlinear response function.[15] The time ordering—in combination with "filter" of the matter system—yields different types of correlation functions, depending on the chosen experimental setup. These include the normally ordered correlation functions of Glauber's theory, which give rise to the $g^{(2)}$-measurement, for instance, in two-photon absorption measurements.[7,16] Consequently, such measurements may equally reveal information on the incident photonic state, such as time-energy entanglement,[17,18] provided that the sample

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response function is known. Moreover, as will be shown below, response functions associated with Raman transitions reveal information, which is not accessible in the standard photon counting experiments.

To set the stage, let us first briefly outline the photon counting formalism. We shall be concerned with the characterization of broadband, ultrafast fields. We thus write the dimensionless field operator as a sum over pulsed modes, $E_A(t) = \sum_k \psi_A^{(k)}(t) A_k$, where the time amplitudes $\psi_A^{(k)}(t)$ form an orthonormal set.[19,20] Clearly, this representation is not unique and will be specified later in the paper.

Detector response times are typically much slower than pulse durations; therefore, the measured observables are time-integrated. In our formalism, the photon number operator then reads

$$n_A = \int dt\, E_A^\dagger(t) E_A(t) = \sum_k A_k^\dagger A_k, \tag{1}$$

which is independent of the choice of the basis $\psi_A^{(k)}$. The correlation between the field A and a second field B, which we write analogously as $E_B(t) = \sum_k \psi_B^{(k)}(t) B_k$, may then be recast in terms of correlation functions of the number operator by the $g^{(2)}$-function,

$$g_{\mathrm{PC}}^{(2)} = \frac{\langle n_A n_B \rangle}{\langle n_A \rangle \langle n_B \rangle} = \frac{\left\langle \sum_{k,k'} A_k^\dagger B_{k'}^\dagger A_k B_{k'} \right\rangle}{\left\langle \sum_k A_k^\dagger A_k \right\rangle \left\langle \sum_k B_k^\dagger B_k \right\rangle}, \tag{2}$$

where we introduced the subscript "PC" (=photon counting) to distinguish it from the Raman correlation function to be defined below. This correlation function can be detected in coincidence measurements, as sketched in Fig. 1(a), where the two fields are separated with a beam splitter, and then measured in the coincidence experiment. This setup implies that the fields E_A and E_B commute, $[A_k, B_k^\dagger] = 0$. The correlation function $g_{\mathrm{PC}}^{(2)}$ can be used to, e.g., measure the cooperativity parameter, i.e., the effective number of entangled modes, or the optical gain in parametric downconversion.[21]

We now demonstrate how Raman transitions give rise to correlation functions different from Eq. (2). To this end, we consider the two-photon process depicted in Fig. 1(b): A high-energy vibrational state g' (in the sense that it is unoccupied in thermal equilibrium) is coupled to the system's ground state g via an off-resonant Raman process. The population in g' is read out through some other process, such as the fluorescence or transient absorption of an additional probe, in which case our observable is given by the population in g' after the interaction with the pulses. This requires the lifetime of g' to be long enough to enable an optical readout of its population. Due to selection rules, g' cannot be dipole-coupled to the ground state g. Hence, it can only decay through slow, nonradiative decay channels.

We write the dipolar light–matter interaction Hamiltonian in the interaction picture with respect to the material and light field Hamiltonians as

$$H_{int}(t) = V(t) E^\dagger(t) + h.c., \tag{3}$$

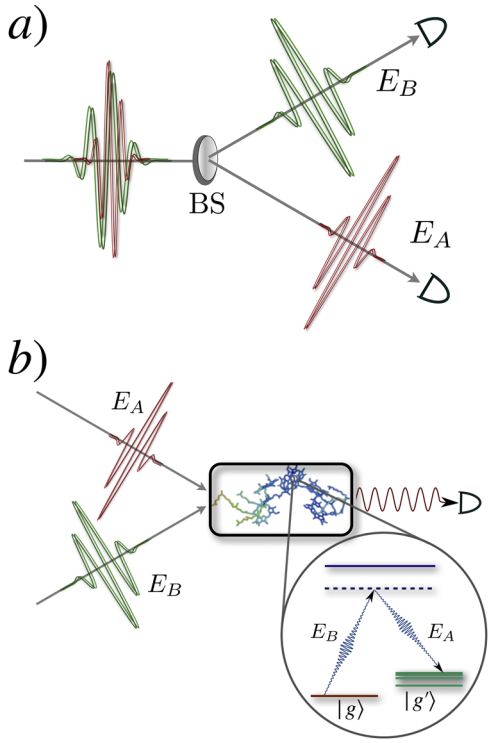

FIG. 1. (a) Measurement of the photon coincidence signal (2): The two fields E_A and E_B are separated at a beam splitter (BS) and detected in coincidence. (b) Measurement of the Raman correlation function (14) via off-resonant Raman scattering: The two fields E_A and E_B drive a Raman transition in a molecule. The created excited state $|g'\rangle$ is then detected by other means, e.g., transient absorption, fluorescence detection, and so on.

where V denotes the positive-frequency component of the material dipole operator, describing the annihilation of excitations in the material, and $E^\dagger$ denotes the negative-frequency component of the electric field operator, corresponding to the creation of photons. In writing Eq. (3), we have also employed the rotating wave approximation. To leading order perturbation theory in the light–matter interaction, the population in g' is given by (see, e.g., Ref. 22)

$$\begin{aligned} p_{g'}(t;\Gamma) = \left(-\frac{i}{\hbar}\right)^4 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{t} d\tau_2' \int_{t_0}^{\tau_2'} d\tau_1' \\ \times \left\langle V(\tau_1') V^\dagger(\tau_2') P_{g'}(t) V(\tau_2) V^\dagger(\tau_1) \right\rangle \\ \times \left\langle E_A^\dagger(\tau_1') E_B(\tau_2') E_B^\dagger(\tau_2) E_A(\tau_1) \right\rangle, \end{aligned} \tag{4}$$

where $P_{g'} = |g'\rangle\langle g'|$ is the projector onto state g'. We consider off-resonant Raman transitions,[23] in which case we may express the transition probabilities in terms of polarizabilities,[24]

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$$p_{g'}(t;\Gamma) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau \int_{t_0}^{t} d\tau' \left\langle \alpha^\dagger(\tau') P_{g'}(t) \alpha(\tau) \right\rangle \times \left\langle E_B^\dagger(\tau') E_A(\tau') E_A^\dagger(\tau) E_B(\tau) \right\rangle \tag{5}$$

$$= \left(-\frac{i}{\hbar}\right)^2 |\alpha_{gg'}|^2 \int_{t_0}^{t} d\tau \int_{t_0}^{t} d\tau' e^{i\omega_{g'}(t-\tau')} e^{-i\omega_{g'}(t-\tau)} \times \left\langle E_B^\dagger(\tau') E_A(\tau') E_A^\dagger(\tau) E_B(\tau) \right\rangle. \tag{6}$$

The population in $p_{g'}$ may be expressed as the modulus square of transition amplitude operators acting on the field Hilbert space, $p_{g'}(t;\Gamma) = \left\langle |T_{g'g}(t)|^2 \right\rangle$, with the transition amplitude operator

$$T_{g'g}(t) = -\frac{i\alpha_{g'g}}{\hbar} \int_{t_0}^{t} d\tau \, e^{i\omega_{g'}\tau} E_A^\dagger(\tau) E_B(\tau), \tag{7}$$

where $\alpha_{g'g}$ denotes the polarizability of the $g - g'$ transition and $\omega_{g'}$ denotes its transition frequency. We only consider times t long after the pulses have passed through the sample. In this case, the populations are constant, and we can extend the time integration in Eq. (7) to infinity.[25,26] Decomposing the two fields in the Schmidt modes introduced above, the transition amplitude simplifies to

$$T_{g'g}(t) = \sum_{k,k'} d_{kk'} A_k^\dagger B_{k'} \tag{8}$$

with

$$d_{kk'} = -\frac{i\alpha_{g'g}}{\hbar} \int_{-\infty}^{\infty} d\tau \, e^{i\omega_{g'}\tau} \psi_A^{(k)}(\tau) \psi_B^{*(k')}(\tau). \tag{9}$$

It follows from Eq. (9) that Raman scattering mixes different modes in beams A and B. This can be simplified by making further assumptions: by choosing a basis in B, which is shifted by $\omega_{g'}$ with respect to A,

$$\psi_A^{(k)}(t) = \psi_B^{(k)}(t) e^{-i\omega_{g'}t}, \tag{10}$$

the time integration simply yields a delta-function, $d_{kk'} = -\frac{i\alpha_{g'g}}{\hbar}\delta_{kk'}$. Hence, apart from an irrelevant prefactor, the Raman transition may be described by the two-photon field operator

$$T = \sum_k A_k^\dagger B_k. \tag{11}$$

In addition, we require the phonon frequency $\omega_{g'}$ to be larger than the bandwidth of the pulses such that the field operators commute, $[A_k, B_k^\dagger] = 0$. The basis $\psi_A^{(k)}$ may still be chosen such as to simplify the description of a particular quantum state. Yet once we pick this basis, it also fixes the corresponding basis for field B. The anti-Stokes process, in which a phonon is destroyed, $\sim A_k B_k^\dagger$ can be neglected since the vibrational state is not excited thermally.

In contrast to intensity measurements, Eq. (1), Raman signals correlate the corresponding high-energy destruction of a photon in mode B (i.e., the positive frequency component of mode B) with a photon creation in mode A (with its negative frequency component). To appreciate the difference, let us first calculate the expectation value of the Raman transition operator T when both fields A and B are in coherent states and temporal amplitudes $\alpha_{A/B}(t)$. By expanding these amplitudes in terms of the eigenmodes $\psi_{A/B}^{(k)}$, we find

$$\langle T \rangle_{coh} = \int dt \, \alpha_A^*(t) \alpha_B(t). \tag{12}$$

Hence, the Raman transition operator quantifies the overlap between two fields' modes. In contrast to Eq. (1), it is inherently phase-dependent. The introduction of a time delay between the two fields will quickly erode this overlap. In the following, we turn to question of how this phase-dependence is reflected in Raman-based photon correlation measurements.

The vibrational population created by the Raman transition is described by the modulus square of the Raman operator (11), which is normalized by the two fields' mean photon numbers,

$$g_{\mathrm{RC}}^{(2)} \equiv \frac{\langle T^\dagger T \rangle}{\langle \sum_k A_k^\dagger A_k \rangle \langle \sum_k B_k^\dagger B_k \rangle} \tag{13}$$

$$= \frac{1}{\langle \sum_k A_k^\dagger A_k \rangle} + \frac{\sum_{k,k'} \langle A_k^\dagger B_{k'}^\dagger A_{k'} B_k \rangle}{\langle \sum_k A_k^\dagger A_k \rangle \langle \sum_k B_k^\dagger B_k \rangle}. \tag{14}$$

In the second line, Eq. (14), we have normally ordered the numerator of Eq. (13). Consequently, the first term stems from the field commutator, and the second term stems from the normally ordered contribution. We find that the off-resonant Raman detection (11) yields a different pairing of operators A_k and B_k in the second term of Eq. (14) compared to two-photon counting (2). This unusual pairing correlates positive frequency contributions from one field with negative frequency parts of the other field, which in turn has important consequences for the information about the quantum state of light that can be obtained with this type of measurement.

To illustrate the information provided by Raman signals compared to conventional photon counting, we now construct input states, which will then be analyzed with either photon counting or Raman measurements. In particular, we consider two fields created by frequency conversion (FC):[27] An initial state $|\phi\rangle_A$ in beam A interacts with a (narrowband) pump pulse via a $\chi^{(2)}$-nonlinearity to populate a new field C, which is shifted by the pump frequency with respect to the initial state, to create the output state $|\phi_{\mathrm{out}}\rangle = \exp(-iH_{\mathrm{FC}})|\phi\rangle_A$. The FC Hamiltonian reads[21,27]

$$H_{\mathrm{FC}} = \int d\omega_a \int d\omega_b \, f_{\mathrm{FC}}(\omega_a, \omega_b) a_{\omega_a}^\dagger b_{\omega_b} + H.c. \tag{15}$$

Here, $a_\omega^\dagger$ (b_ω) denotes the photon (annihilation) creation operator in field A (B), respectively, and f_{PDC} is the phase-matching function of the FC process that depends on the crystal properties and the pump field (see, e.g., the discussion in Ref. 27). The discussion of its properties becomes most transparent by using the Schmidt decomposition of the phase-matching function[19]

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$$f_{\mathrm{FC}}(\omega_a,\omega_b) = \sum_k \tilde{r}_k \psi_A^{(k)}(\omega_a)\psi_B^{*(k)}(\omega_b), \tag{16}$$

where $\tilde{r}_k > 0$ gives the weight, with which mode k participates in the FC process, and the functions $\{\psi_A^{(k)}\}$ and $\{\psi_B^{(k)}\}$ are sets of orthonormal functions, which depend on the phase-matching conditions inside the nonlinear crystal.[28–30] These define the basis set, for which the Raman correlation function (14) can be evaluated most easily.

With the initial state $|\phi\rangle_A \otimes |0\rangle_B$, the output state in the weak conversion limit, when only one photon is exchanged between the two fields, may be written as

$$|\phi_{\mathrm{out}}\rangle = \sum_k r_k A_k|\phi\rangle_A \otimes B_k^\dagger|0\rangle_B, \tag{17}$$

where we introduce renormalized mode weights r_k, satisfying $\langle\phi_{\mathrm{out}}|\phi_{\mathrm{out}}\rangle = \sum_k r_k^2\langle\phi|A_k^\dagger A_k|\phi\rangle = 1$. Note that due to the normalization, the factors r_k depend on the input state coefficients c_k [see, for example, Eq. (19) below]. This state cannot generally be factorized. However, when we calculate the conventional cross correlation function (2), we obtain

$$g_{\mathrm{PC}}^{(2)} = 1, \tag{18}$$

regardless of the input state $|\phi\rangle$ or the structure of the FC process. Hence, photon counting does not provide information on the properties of state (17). In contrast, the Raman correlation function does. In the following, we will consider several states of light, where the Raman correlation provides new information. Our first example will be a coherent state of the form

$$|\phi\rangle_A = \prod_k \exp\left(c_k A_k^\dagger - c_k^* A_k\right)|0\rangle_A, \tag{19}$$

with $\sum_k |c_k|^2 = 1$, such that $\langle\sum_k A_k^\dagger A_k\rangle = \langle\sum_k B_k^\dagger B_k\rangle = 1$; we arrive at

$$g_{\mathrm{RC}}^{(2)} = 1 + \left(\sum_k r_k|c_k|^2\right)^2, \tag{20}$$

which depends on both initial states as well as the FC process. Hence, while photon counting cannot reveal any properties of the frequency conversion process, Raman measurements do. Let us first assume that the input state (19) has a large bandwidth with $c_k = 1/\sqrt{M}$ for $k \le M$. If the FC only affects a single mode k_0, i.e., $r_{k_0} = const$, and = 0 otherwise, we obtain the limiting value for the correlation function $g_{\mathrm{FC}}^{(2)} \to 1 + 1/M$. If, on the other hand, many modes participate in the FC process, $r_k = const$ for $k \le M$, we obtain $g_{\mathrm{FC}}^{(2)} \to 2$.

This behavior is illustrated in Fig. 2, where we simulate the Raman correlation function $g_{\mathrm{RC}}^{(2)}$ using a bi-Gaussian phase-matching function $f_{\mathrm{FC}}(\omega_a,\omega_b) = \alpha \exp[-\omega^2/(2\sigma_p^2)]\exp[-\gamma(\Delta k(\omega_a,\omega_b)L/2)^2]/\sqrt{2\pi\sigma_p^2}$, where $\Delta k(\omega_a,\omega_b)L = -(\omega_a - \omega_1 - \omega_p)T_1 + (\omega_b - \omega_1)T_2$ describes the phase-matching in the crystal by the two inverse bandwidths T_1 and T_2, and σ_p describes the pump bandwidth. In this case, the Schmidt decomposition (16) can be carried out analytically, and the eigenmodes are simply given by Hermite functions.[25,26]

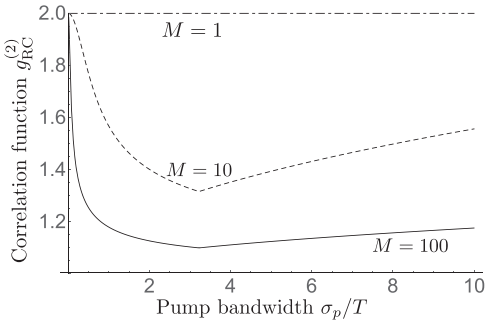

FIG. 2. Variation of the Raman correlation function $g_{\mathrm{RC}}^{(2)}$, Eq. (20), with the pump bandwidth σ_p measured in units of the inverse characteristic time scale T_1 of the FC process. The parameter M denotes the number of Schmidt modes involved in the Raman process [see the discussion following Eq. (20)].

We depict the dependence of the Raman correlation function $g_{\mathrm{RC}}^{(2)}$ on the number of modes in the FC process (16) for different coherent input states. The FC process is controlled by the bandwidth σ_p of the pump pulse facilitating the FC, and the input state is described by $c_k = 1/\sqrt{M}$ for $k \le M$. For $M = 100$, $g_{\mathrm{RC}}^{(2)}$ is close to two only for $\sigma_p \times T_1 \ll 1$, i.e., when the pump bandwidth is much smaller than that of the frequency converted pulse $\sim 1/T_1$. In this case, many modes contribute to the FC process. As soon as the bandwidths are comparable, $\sigma_p \times T_1 \sim 1$, the correlation function drops to ~1.1 and $\sigma_p/T \sim 3$ and then slowly rises again. For $M = 10$, the Raman correlation function $g_{\mathrm{RC}}^{(2)}$ shows a very similar behavior, yet less pronounced. It drops to 1.4 since only the behavior of the ten largest eigenvalues contributes to the signal. This may be explained by the close analogy between the FC Hamiltonian and the well studied Hamiltonian for parametric down conversion. If the pump bandwidth is much smaller than the pulse bandwidth, $\sigma_p \ll 1/T_1$, the outgoing light is strongly anti-correlated, while for $\sigma_p \gg 1/T_1$, it shows strong positive correlations.[31] For intermediate values of σ_p, the correlations naturally move through zero.

In our discussion so far, state (17) is separable and hence shows no quantum correlations. This is no longer the case when the input state to Eq. (17) is entangled. In this situation, we may write the input state, e.g., for the case of a type-I downconverted photon pair as

$$|\phi\rangle_A = \frac{1}{\sqrt{2}}\sum_{k_1,k_2} d_{k_1,k_2} A_{k_1}^\dagger A_{k_2}^\dagger|0\rangle, \tag{21}$$

where the symmetric coefficient matrix $d_{k_1k_2}$ stems from the decomposition of the two-photon wavefunction in the eigenbasis of the FC process [Eq. (16)]. A similar calculation to before yields

$$g_{\mathrm{RC}}^{(2)} = 1 + 2\sum_{k_1,k_2} r_{k_1} r_{k_2}|d_{k_1,k_2}|^2. \tag{22}$$

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Hence, the Raman correlation function in this case is again controlled by the FC process as described by the coefficients r_k. However, it further depends on the two-photon wavefunction and hence on the entanglement of the two photons. The Raman measurement contains information on the nonseparability of state (17), which is missed by the two-photon counting measurements [see Eq. (18)].

To conclude, we have proposed that Raman measurements provide a tool for the characterization of the quantum state of multimode light and demonstrated that it offers complementary information content to the well-established photon counting formalism. As an example, we demonstrated how the multimode structure in a quantum state of light created by a frequency conversion process may be detected. We envision that such measurements might be particularly interesting for multimode, broadband fields considered here, where direct quantum state tomography becomes prohibitively expensive.

Our results point out the potential of nonlinear optical signals in the quantum regime as photon detectors: By replacing the two-level atoms of Glauber's theory with more complex level detectors, additional information on the quantum state of the light may be extracted. The full extent to this approach to the characterization of multimode light fields has yet to be explored. The present formalism based on a quantum state that is generated as the result of $\chi^{(2)}$ nonlinear frequency conversion. For optical wavelengths of the fields A and B, the pump must be in the IR regime to facilitate the phase-matching. This, in principle, is limiting the spectral resolution and the degree of frequency correlations that are governed by σ_p. An alternative approach can utilize the $\chi^{(3)}$ nonlinearity in the four-wave-mixing conversion process.[38] This way all four fields are in the optical regime and the corresponding degree of correlations can be maintained with higher precision than in the $\chi^{(2)}$ case.

Conversely, the discussion of quantum properties of light in Raman transitions opens the possibility of exploiting quantum correlations in Raman spectroscopy. A connection should be established to older investigations into the role of photon fluctuations in stimulated Raman processes.[32–34] The output state (17) obtained from an entangled input state (21) could be understood as an entangled state of a photon with a photon hole,[35,36] and our result shows that such entanglement is reflected in Raman measurements. Future work will explore how these correlations may be tailored to control spectroscopic signals.[37]

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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