Enhancement of Stokes–anti-Stokes correlations by the classical incoherent incident light

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It is known that spontaneous Raman scattering is accompanied by the appearance of nonclassical cross correlations of photons at Stokes and anti-Stokes frequencies. Such correlations occur due to the internal nonlinear interaction between electronic and nuclear vibration degrees of freedom. Since the properties of a given media are unchangeable, the possibilities for controlling the cross correlations are limited. This, in turn, restricts the possible applications of the correlated light obtained during the spontaneous Raman scattering. In this work, we investigate the influence of statistical properties of an incident light on the cross correlations of Stokes and anti-Stokes light. We show that the incoherence of the incident light results not only in the incoherence of the scattered light but also in the enhancement of the interbeam coherence at different frequencies. We demonstrate that the cross correlations of Stokes and anti-Stokes light intensities are enhanced when the incident light with high second-order autocorrelation function is applied. Our results pave the way to control correlated light obtained in the process of spontaneous Raman scattering.

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I. INTRODUCTION

Raman scattering of light is a powerful and widespread tool for quantitative analysis of the composition of substances, which has been used for more than 50 years [1–3]. In addition to the spectroscopic applications, it was revealed that the scattered light obtained from spontaneous Raman scattering may exhibit quantum correlations [4,5]. In this case, the cross correlations of Stokes and anti-Stokes light can exceed the classical limit [4,5]. The latter means that the product of second-order coherence functions at the Stokes and anti-Stokes frequencies, $g^{(2)}_{\mathrm{St,St}} = \langle \hat{a}^\dagger_{\mathrm{St}} \hat{a}^\dagger_{\mathrm{St}} \hat{a}_{\mathrm{St}} \hat{a}_{\mathrm{St}} \rangle / \langle \hat{a}^\dagger_{\mathrm{St}} \hat{a}_{\mathrm{St}} \rangle^2$ and $g^{(2)}_{\mathrm{aSt,aSt}} = \langle \hat{a}^\dagger_{\mathrm{aSt}} \hat{a}^\dagger_{\mathrm{aSt}} \hat{a}_{\mathrm{aSt}} \hat{a}_{\mathrm{aSt}} \rangle / \langle \hat{a}^\dagger_{\mathrm{aSt}} \hat{a}_{\mathrm{aSt}} \rangle^2$, is less than the square of the cross correlation $g^{(2)}_{\mathrm{St,aSt}} = \langle \hat{a}^\dagger_{\mathrm{St}} \hat{a}^\dagger_{\mathrm{aSt}} \hat{a}_{\mathrm{aSt}} \hat{a}_{\mathrm{St}} \rangle / \langle \hat{a}^\dagger_{\mathrm{aSt}} \hat{a}_{\mathrm{aSt}} \rangle \langle \hat{a}^\dagger_{\mathrm{St}} \hat{a}_{\mathrm{St}} \rangle$ from the Stokes and anti-Stokes components, i.e., the following inequality holds: $g^{(2)}_{\mathrm{St,St}} g^{(2)}_{\mathrm{aSt,aSt}} < (g^{(2)}_{\mathrm{St,aSt}})^2$. Experimental studies of this phenomenon showed that nonclassical correlations of Stokes and anti-Stokes light are observed when light is scattered on diamond [6–11], water [12,13], organic molecules [14], and other substances [13,15,16], as well as micromechanical systems [17,18]. Nonclassical correlations of Raman light emerge in waveguides [19–22]. Moreover, in experiments on spontaneous Raman scattering of light in a silicon waveguide [23], it was shown that nonclassical cross correlations can occur between Stokes light and phonons in the waveguide. In the above experimental works [19,20,23] it was noted that a necessary condition for observation is a small number of phonons (vibrons) excited by temperature fluctuations of the environment [7].

Correlations of Stokes and anti-Stokes light can be measured with a Hanbury-Brown-Twiss setup [4,24]. Nonclassical correlations of Stokes and anti-Stokes light manifest themselves in this type of experiment as an anomalously large number of the simultaneously triggered Stokes and anti-Stokes photon detectors [6–8,12–14]. This means that Stokes and anti-Stokes photons are produced in pairs during spontaneous Raman scattering. The pair production of Stokes and anti-Stokes photons during spontaneous Raman scattering can be used in heralded light sources [15,25,26] as an alternative to spontaneous parametric down conversion [4,27]. Such sources are used, for example, for ghost imaging [28–31]. The ability to generate photon pairs is also important for other applications [32], such as heralded single photon sources [33–40], increasing the visibility of two-photon interferometry [41,42], increasing the visibility of the Hong-Ou-Mandel interference [43–45], increasing the visibility in measurements of entanglement [46,47], and preparation of the Fock states [15]. Note that correlation between different frequency components arises when the electromagnetic (EM) field is irradiated by the optically pumped gaseous medium in the presence of magnetic field which creates Zeeman splitting [48,49].

It should be emphasized that in the number of applications, the interbeam second-order coherence function is important by itself regardless of how large it is compared with the multiplication of the single frequency second-order coherence functions. For example, the increase of the visibility of interferometry depends on the absolute value of correlations of Stokes and anti-Stokes light, i.e., on $g^{(2)}_{\mathrm{St,aSt}}$, while the nonclassicality of the cross correlations by itself is not significant [41–45,50].

It is usually assumed that the value $g^{(2)}_{\mathrm{St,aSt}}$ is determined only by the properties of the substance and cannot be changed. In this paper, we show that it is not so. We demonstrate that, in addition to the properties of a substance, the quantity $g^{(2)}_{\mathrm{St,aSt}}$ depends on the statistical properties of the incident light. We show that an increase in the second-order autocorrelation function of the incident light enhances the cross correlations of the Stokes and anti-Stokes scattered light. To this end, we develop an approach to the description of spontaneous Raman scattering of light on molecules based on the Heisenberg-Langevin equations. We find an approximate solution to these equations and show how this solution reproduces the known properties of spontaneous Raman scattering, namely, the spectrum of Stokes and anti-Stokes signals, as well as the statistics of scattered light. Next, we show how the statistics of an incident light influence the Stokes–anti-Stokes second-order cross correlations. The obtained results pave the way to control the statistical properties of the photon pairs obtained in the process of Raman scattering.

II. DESCRIPTION OF THE MODEL

We consider a molecule affected by an incident EM field. To describe the dynamics of such a system, we will use the model developed in [51,52]. Namely, we describe the electronic subsystem of the molecule as an effective two-level system (TLS). We describe the vibrational subsystem of the molecule as a harmonic oscillator and neglect the anharmonicity of the oscillations of the nuclei in the molecule. We describe the interaction of the electronic and vibrational subsystems of the molecule by the Fröhlich Hamiltonian [53]. For simplicity, we assume that the external field interacts only with the electronic subsystem of the molecule and does not interact directly with the nuclear subsystem. The Hamiltonian of the system under consideration in the rotating wave approximation has the form [54–60]

$$\begin{aligned}\hat{H}_S &= \hbar\omega_0\hat{\sigma}^\dagger\hat{\sigma} + \hbar\omega_{\mathrm{v}}\hat{b}^\dagger\hat{b} + \hbar g\hat{\sigma}^\dagger\hat{\sigma}(\hat{b}^\dagger + \hat{b})\\ &\quad + \hbar\hat{\Omega}(t)(\hat{\sigma}^\dagger e^{-i\omega_\Omega t} + \hat{\sigma}e^{i\omega_\Omega t}),\end{aligned} \tag{1}$$

where ω_Ω, ω_0, and ω_{v} are the central frequency of the external field, the transition frequency of the TLS, and the eigenfrequency of vibration of the nuclei of the molecule, respectively. Following the experimentally feasible parameter range [12–16], we consider the nonresonant scattering on the molecule, i.e., we suppose that $|\omega_0 - \omega_\Omega| \gg \gamma_\perp$, where $\gamma_\perp$ is the rate of transverse relaxation of the TLS. The operators $\hat{\sigma}$ and $\hat{\sigma}^\dagger$ are the operators of the TLS transition, the operators $\hat{b}$ and $\hat{b}^\dagger$ are the raising and lowering operators for the vibrational subsystem of the molecule, and g is the constant of the interaction of the TLS and the vibrations of the nuclei of the molecule. The operator of the TLS dipole moment $\hat{\boldsymbol{d}}$ and the amplitude operator of the vibrations of the nuclei of the molecule $\hat{x}$ are connected with the operators $\hat{\sigma}$ and $\hat{b}$ through the equalities $\hat{\boldsymbol{d}} = \boldsymbol{d}_{\mathrm{eg}}(\hat{\sigma} + \hat{\sigma}^\dagger)$ and $\hat{x} = x_0(\hat{b} + \hat{b}^\dagger)$, where $\boldsymbol{d}_{\mathrm{eg}}$ is the dipole moment of the TLS transition and $x_0 = \sqrt{\hbar/2m\omega_{\mathrm{vib}}}$ is the quantum of the molecule vibration amplitude. Thus, the operators $\hat{\sigma}$ and $\hat{b}$ have the physical meaning of dimensionless amplitudes of electric dipole moment and nuclei oscillations, respectively. The last term in Hamiltonian (1) describes the interaction of an external field with a molecule, $\hat{\Omega}(t) = -\boldsymbol{d}_{\mathrm{eg}} \cdot \hat{\boldsymbol{E}}(t)/\hbar$ represents the Rabi frequency of this interaction, and $\hat{\boldsymbol{E}}(t)$ is the amplitude of the electric field of the incident light at the location of the molecule.

Let us consider in more detail the properties of an external light source. We consider a stationary external source with a spectrum width Γ_1, and a central frequency ω_Ω. To describe such a light source, we assume that the field amplitude of an external source $\hat{\Omega}(t)$ is an operator with a average $\langle\hat{\Omega}(t)\rangle = \Omega(t)$, and with the first-order two-time correlation function

$$\langle\hat{\Omega}^\dagger(t)\hat{\Omega}(t+\tau)\rangle = I\exp(-\Gamma_1\tau), \quad \tau \geqslant 0, \tag{2}$$

where $I(t) \equiv \langle\hat{\Omega}^\dagger(t)\Omega(t)\rangle$ is proportional to the intensity of the external source. For the ideally coherent light source $|\Omega(t)|^2 = I$ and $\Gamma_1 = 0$, while for incoherent light $\langle\hat{\Omega}(t)\rangle = 0$. We assume that the autocorrelation function of an external source $g^{(2)}_\Omega(\tau)$ is

$$\begin{aligned}g^{(2)}_\Omega(\tau) &= \frac{\langle\hat{\Omega}^\dagger(t)\hat{\Omega}^\dagger(t+\tau)\hat{\Omega}(t+\tau)\hat{\Omega}(t)\rangle}{\langle\hat{\Omega}^\dagger(t)\hat{\Omega}(t)\rangle\langle\hat{\Omega}^\dagger(t+\tau)\hat{\Omega}(t+\tau)\rangle}\\ &= \big(g^{(2)}_\Omega(0) - 1\big)e^{-\Gamma_2|\tau|} + 1.\end{aligned} \tag{3}$$

This means that the equal-time second-order autocorrelation function of an external source is equal to $g^{(2)}_\Omega(0)$ and drops to unity with a characteristic time Γ_2^{-1}. We assume that the spectrum width of the external source is much smaller than the detuning of the frequency of the external field from the frequency of the electronic transition of the molecule, $|\omega_0 - \omega_\Omega| \gg \Gamma_1, \Gamma_2$. For the incident light with finite linewidth and nonzero $\langle\Omega\rangle$, Eq. (2) changes to $\langle\hat{\Omega}^\dagger(t)\hat{\Omega}(t+\tau)\rangle = I\exp(-\Gamma_1\tau) + I_0$ with $I_0 = |\langle\Omega\rangle|^2$, but Eq. (3) remains the same. As we will see below, this affects the spectrum of scattered light (see Sec. III), but does not affect its statistical properties.

The relaxation processes in a molecule are due to the interaction with reservoirs described by the Hamiltonian

$$\begin{aligned}\hat{H}_{\mathrm{Res}} &= \sum_{\mathbf{k},\mu}\hbar\omega_{\mathbf{k}}\hat{a}^\dagger_{\mathbf{k},\mu}\hat{a}_{\mathbf{k},\mu} + \sum_k\hbar\omega_{\mathrm{dp}k}\hat{c}^\dagger_{\mathrm{dp}k}\hat{c}_{\mathrm{dp}k}\\ &\quad + \sum_k\hbar\omega_{\mathrm{m}k}\hat{c}^\dagger_{\mathrm{m}k}\hat{c}_{\mathrm{m}k}.\end{aligned} \tag{4}$$

The first term describes the reservoir of EM field of the empty space, and $\hat{a}^\dagger_{\mathbf{k},\mu}$ and $\hat{a}_{\mathbf{k},\mu}$ are photon creation and annihilation operators with the wave vector $\mathbf{k}$ and polarization μ. The second term corresponds to the dephasing reservoir that is described by the operators $\hat{c}^\dagger_{\mathrm{dp}k}$ and $\hat{c}_{\mathrm{dp}k}$. This reservoir is responsible for the relaxation of phase of the electronic subsystem. The third term is the reservoir which is responsible for the relaxation of the vibron mode $\hat{b}$ of the molecule [61–64].

The interaction of the system with the reservoirs is described by the Hamiltonian

$$\begin{aligned}\hat{H}_{\mathrm{SRes}} &= \sum_{\mathbf{k},\mu}\boldsymbol{E}_{\mathbf{k},\mu}\cdot\boldsymbol{d}_{\mathrm{eg}}(\hat{a}^\dagger_{\mathbf{k},\mu} + \hat{a}_{\mathbf{k},\mu})(\hat{\sigma}^\dagger + \hat{\sigma})\\ &\quad + \sum_k\hbar\kappa_{\mathrm{dp}k}(\hat{c}^\dagger_{\mathrm{dp}k} + \hat{c}_{\mathrm{dp}k})\hat{\sigma}^\dagger\hat{\sigma}\\ &\quad + \sum_k\hbar\kappa_{\mathrm{m}k}(\hat{c}^\dagger_{\mathrm{m}k} + \hat{c}_{\mathrm{m}k})(\hat{b}^\dagger + \hat{b}),\end{aligned} \tag{5}$$

where $\kappa_{\mathrm{dp}k}$ and $\kappa_{\mathrm{m}k}$ are the respective interaction constants, and $\boldsymbol{E}_{\mathbf{k},\mu}$ is the quantum of the electric field of a photon with the wave vector $\mathbf{k}$ and polarization μ.

In the Born-Markov approximation it is possible to eliminate reservoir degrees of freedom [5,65]. To do this it is necessary to suppose that the reservoir is in the thermal equilibrium at the fixed temperature and the interaction between the system and the reservoirs is weak. From Hamiltonians (1), (4), and (5) one can obtain the following Heisenberg-Langevin operator equations [5,25] for the operator of the dipole moment of the TLS $\hat{\sigma}$ and for the operator of the amplitude of vibration of the nuclei of a molecule $\hat{b}$ [51,52]:

$$d\hat{\sigma}/dt = (-i\omega_0 - \gamma_\perp)\hat{\sigma} + i(2\hat{\sigma}^\dagger\hat{\sigma} - 1)\hat{\Omega}(t)e^{-i\omega_\Omega t} - ig\hat{\sigma}(\hat{b}^\dagger + \hat{b}) + \hat{F}_\sigma(t), \tag{6}$$

$$d\hat{b}/dt = (-i\omega_{\mathrm{v}} - \gamma_{\mathrm{v}})\hat{b} - ig\hat{\sigma}^\dagger\hat{\sigma} + \hat{F}_b(t), \tag{7}$$

where γ_{v} is the damping rate of the vibrations of the nuclei of the molecule, and $\hat{F}_\sigma(t)$ and $\hat{F}_b(t)$ are the thermal noise acting on the vibrational degree of freedom of the molecule and on the dipole moment of the electronic transition from the environment. The value of dissipation constant $\gamma_\perp$ is determined by the processes of energy and phase relaxation, i.e., $\gamma_\perp = \gamma_{\mathrm{en}} + \gamma_{\mathrm{ph}}$. We note that the dissipation rate of the dipole moment $\gamma_\perp$ for many molecules is mainly determined by the dephasing processes [66], such that $\gamma_\perp \simeq \gamma_{\mathrm{ph}}$. Thermal noises are not arbitrary, but are associated with losses in the system through the fluctuation-dissipation theorem [5,67]. Namely, noises $\hat{F}_b(t)$ and $\hat{F}_\sigma(t)$ have the following correlation properties

$$\langle\hat{F}_b(t)\rangle = 0, \quad \langle\hat{F}_\sigma(t)\rangle = 0, \tag{8}$$

$$\langle\hat{F}_b(t_1)\hat{F}_b(t_2)\rangle = 0, \quad \langle\hat{F}_\sigma(t_1)\hat{F}_\sigma(t_2)\rangle = 0, \tag{9}$$

$$\langle\hat{F}_b^\dagger(t_1)\hat{F}_b^\dagger(t_2)\rangle = 0, \quad \langle\hat{F}_\sigma^\dagger(t_1)\hat{F}_\sigma^\dagger(t_2)\rangle = 0, \tag{10}$$

$$\langle\hat{F}_b^\dagger(t_1)\hat{F}_b(t_2)\rangle = 2\gamma_{\mathrm{v}} n_{\mathrm{v}}\delta(t_1 - t_2), \tag{11}$$

$$\langle\hat{F}_\sigma^\dagger(t_1)\hat{F}_\sigma(t_2)\rangle = \gamma_{\mathrm{ph}}\langle\hat{\sigma}^\dagger\hat{\sigma}\rangle\delta(t_1 - t_2), \tag{12}$$

where $n_{\mathrm{v}} = [\exp(\hbar\omega_{\mathrm{v}}/T) - 1]^{-1}$ and T is the temperature of the environment. We consider the case of a weak population of the upper level of the electron subsystem, $\langle\hat{\sigma}^\dagger\hat{\sigma}\rangle \sim I/|\omega - \omega_0|^2 \ll 1$, which is typical in experiments on nonresonant Raman scattering, therefore in Eq. (6) we neglect the noise acting on the electron subsystem of the molecule. This is valid for the moderate values of the amplitudes of the external pump: $I \leqslant \gamma_{\mathrm{v}} n_{\mathrm{v}}|\omega_\Omega - \omega_0|^2/\gamma_\perp$. For typical parameters $\gamma_{\mathrm{v}} \sim 10^{-4}$ eV, $n_{\mathrm{v}} \sim 10^{-4}$, $|\omega_\Omega - \omega_0| \sim 1$ eV, $\gamma_\perp \sim 10^{-2}$ eV we obtain $\sqrt{I} < 10^{-3}$ eV, which for the electronic transition dipole moment $|\boldsymbol{d}_{\mathrm{eg}}| \sim 10\,\mathrm{D}$ results in the restriction to the incident electric field amplitude $|\boldsymbol{E}(t)| < 10^6$ V/m.

III. DYNAMICS OF THE DIPOLE MOMENT OF A MOLECULE AND STATISTICAL PROPERTIES OF SCATTERED LIGHT

The system (6), (7) cannot be solved exactly. Therefore, we construct a solution to the system of equations (6), (7) according to perturbation theory. There are two small parameters in the system. The first small parameter ε_1 is the ratio of the mean value of modulus of the Rabi frequency $\sqrt{\langle\hat{\Omega}^\dagger(t)\hat{\Omega}(t)\rangle} = \sqrt{I}$ [see Eq. (2)] to the detuning of the frequency of the external field from the transition frequency of the TLS

$$\varepsilon_1 = \frac{\sqrt{I}}{|\omega_\Omega - \omega_0|} \ll 1. \tag{13}$$

The second small parameter ε_2 is the ratio of the constant of the interaction between the electrons and the vibrons of the molecule and the frequency detuning of the incident light from the electronic transition frequency,

$$\varepsilon_2 = \frac{g}{|\omega_\Omega - \omega_0|} \ll 1. \tag{14}$$

To solve the system of Eqs. (6), (7) according to perturbation theory, we expand the operator of the dipole moment of the electronic subsystem of the molecule $\hat{\sigma}(t)$ and the operator of the amplitude of vibration of the nuclei of the molecule $\hat{b}(t)$ in a series in small parameters ε_1 and ε_2. In each order of perturbation theory, we obtain a linear system of operator equation with quantum noise. This linear system can be solved exactly. The solution of the system of Eqs. (6),(7) for the operator of the dipole moment of the electronic subsystem of the molecule $\hat{\sigma}(t)$ up to the order $\varepsilon_1 \cdot \varepsilon_2$ has the form (see Appendix A)

$$\hat{\sigma}(t) \approx \hat{\sigma}_{\mathrm{R}}(t) + \hat{\sigma}_{\mathrm{St}}(t) + \hat{\sigma}_{\mathrm{aSt}}(t). \tag{15}$$

The operator $\hat{\sigma}_{\mathrm{R}}(t)$ represents the contribution to the dipole moment of the molecule which is responsible for Rayleigh scattering

$$\hat{\sigma}_{\mathrm{R}}(t) = \frac{\hat{\Omega}(t)}{\omega_\Omega - \omega_0} e^{-i\omega_\Omega t}. \tag{16}$$

The operators $\hat{\sigma}_{\mathrm{St}}(t)$ and $\hat{\sigma}_{\mathrm{aSt}}(t)$ are the contributions to the dipole moment of the molecule which are responsible for Stokes and anti-Stokes scattering, respectively,

$$\hat{\sigma}_{\mathrm{St}}(t) = \frac{g}{\omega_\Omega - \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_{\mathrm{R}}(t)\hat{b}_{\mathrm{th}}^\dagger(t), \tag{17}$$

$$\hat{\sigma}_{\mathrm{aSt}}(t) = \frac{g}{\omega_\Omega + \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_{\mathrm{R}}(t)\hat{b}_{\mathrm{th}}(t). \tag{18}$$

The operator $\hat{b}_{\mathrm{th}}(t)$ is the operator of the amplitude of vibration of the nuclei of the molecule under the influence of thermal fluctuations of the environment and has the form

$$\hat{b}_{\mathrm{th}}(t) = \int_0^t dt' G_b(t - t')\hat{F}_b(t'), \tag{19}$$

where we have denoted the Green's function for the linearized equation (7) $G_b(\tau) = \exp[(-i\omega_{\mathrm{v}} - \gamma_{\mathrm{v}})\tau]$. Since the vibrations of the nuclei of the molecule (19) occur due to thermal fluctuations of the environment, the average vibration intensity is described by the Bose-Einstein distribution.

Indeed, it follows from the expression for the operator of the vibration amplitude of the nuclei of the molecule (19) and the correlation (11) that

$$\langle \hat{b}_{\mathrm{th}}^{\dagger}(t)\hat{b}_{\mathrm{th}}(t)\rangle = n_{\mathrm{v}} = \frac{1}{e^{\hbar\omega_{\mathrm{v}}/T} - 1}. \tag{20}$$

The expression for the operator of the dipole moment of the molecule (15) allows us to calculate the spectrum of scattered light $S(\omega)$, according to the quantum regression theorem [5,67],

$$S(\omega) = \left|\boldsymbol{d}_{\mathrm{eg}}\right|^2 \mathrm{Re}\int_0^{+\infty} \langle\hat{\sigma}^{\dagger}(t+\tau)\hat{\sigma}(t)\rangle e^{-i\omega\tau}d\tau. \tag{21}$$

Due to the properties of the correlations of thermal noise acting on the nuclei of the molecule, Eqs. (8)–(10), the correlations $\langle\hat{\sigma}_{\mathrm{R}}^{\dagger}(t+\tau)\hat{\sigma}_{\mathrm{St}}(t)\rangle$, $\langle\hat{\sigma}_{\mathrm{R}}^{\dagger}(t+\tau)\hat{\sigma}_{\mathrm{aSt}}(t)\rangle$, and $\langle\hat{\sigma}_{\mathrm{St}}^{\dagger}(t+\tau)\hat{\sigma}_{\mathrm{aSt}}(t)\rangle$ are identically equal to zero. Consequently, the spectrum (21) splits into Rayleigh $[S_{\mathrm{R}}(\omega)]$, Stokes $[S_{\mathrm{St}}(\omega)]$, and anti-Stokes $[S_{\mathrm{aSt}}(\omega)]$ components,

$$S(\omega) = S_{\mathrm{R}}(\omega) + S_{\mathrm{St}}(\omega) + S_{\mathrm{aSt}}(\omega), \tag{22}$$

where

$$S_{\mathrm{R}}(\omega) = |\boldsymbol{d}_{\mathrm{eg}}|^2 \mathrm{Re}\int_0^{+\infty} \langle\hat{\sigma}_{\mathrm{R}}^{\dagger}(t+\tau)\hat{\sigma}_{\mathrm{R}}(t)\rangle e^{-i\omega\tau}d\tau, \tag{23}$$

$$S_{\mathrm{St}}(\omega) = |\boldsymbol{d}_{\mathrm{eg}}|^2 \mathrm{Re}\int_0^{+\infty} \langle\hat{\sigma}_{\mathrm{St}}^{\dagger}(t+\tau)\hat{\sigma}_{\mathrm{St}}(t)\rangle e^{-i\omega\tau}d\tau, \tag{24}$$

$$S_{\mathrm{aSt}}(\omega) = |\boldsymbol{d}_{\mathrm{eg}}|^2 \mathrm{Re}\int_0^{+\infty} \langle\hat{\sigma}_{\mathrm{aSt}}^{\dagger}(t+\tau)\hat{\sigma}_{\mathrm{aSt}}(t)\rangle e^{-i\omega\tau}d\tau. \tag{25}$$

Using Eqs. (16) and (2) we find the spectrum of Rayleigh scattering,

$$S_{\mathrm{R}}(\omega) = S_0\frac{\Gamma_1}{(\omega_\Omega - \omega)^2 + \Gamma_1^2}, \tag{26}$$

where $S_0 = I|\boldsymbol{d}_{\mathrm{eg}}|^2/(\omega_\Omega - \omega_0)^2$. Note that for ideally coherent light $\Gamma_1 = 0$ and Eq. (26) takes the form $S_{\mathrm{R}}(\omega) = S_0\pi\delta(\omega_\Omega - \omega)$ which reproduces the well-known result of coherent nature of Rayleigh scattered light [5]. Similarly to (26), one can find the spectrum of Stokes and anti-Stokes scattered light from Eqs. (17), (18), (11), (12), and (2),

$$S_{\mathrm{St}}(\omega) = S_0\frac{g^2}{(\omega_{\mathrm{St}} - \omega_0)^2}\frac{\Gamma_1 + \gamma_{\mathrm{v}}}{(\omega_{\mathrm{St}} - \omega)^2 + (\Gamma_1 + \gamma_{\mathrm{v}})^2}(1 + n_{\mathrm{v}}), \tag{27}$$

$$S_{\mathrm{aSt}}(\omega) = S_0\frac{g^2}{(\omega_{\mathrm{aSt}} - \omega_0)^2}\frac{\Gamma_1 + \gamma_{\mathrm{v}}}{(\omega_{\mathrm{aSt}} - \omega)^2 + (\Gamma_1 + \gamma_{\mathrm{v}})^2}n_{\mathrm{v}}, \tag{28}$$

where $\omega_{\mathrm{St}} = \omega_\Omega - \omega_{\mathrm{v}}$ and $\omega_{\mathrm{aSt}} = \omega_\Omega + \omega_{\mathrm{v}}$. For the incident light with $\langle\hat{\Omega}^{\dagger}(t)\hat{\Omega}(t+\tau)\rangle = I\exp(-\Gamma_1\tau) + I_0$ Eqs. (16)–(18) do not change. However the spectra of Rayleigh, Stokes, and anti-Stokes scattered light (26)–(28) for such a source have a slightly different form. The explicit expressions for these spectra can be obtained straightforwardly and are not presented here.

The Raman scattering spectra reflect the thermal nature of the vibrations of the nuclei of the molecules. Indeed, it follows from Eqs. (27) and (28) that $S_{\mathrm{St}}(\omega) \propto \langle\hat{b}_{\mathrm{th}}\hat{b}_{\mathrm{th}}^{\dagger}\rangle = 1 + n_{\mathrm{v}}$ and $S_{\mathrm{aSt}}(\omega) \propto \langle\hat{b}_{\mathrm{th}}^{\dagger}\hat{b}_{\mathrm{th}}\rangle = n_{\mathrm{v}}$. Moreover, the calculated spectra of the Stokes and anti-Stokes scattered light (27) and (28) obey the relation

$$\frac{S_{\mathrm{aSt}}(\omega_\Omega + \Delta\omega)}{S_{\mathrm{St}}(\omega_\Omega - \Delta\omega)} = \left(\frac{\omega_{\mathrm{St}} - \omega_0}{\omega_{\mathrm{aSt}} - \omega_0}\right)^2 \times \frac{n_{\mathrm{v}}}{(1 + n_{\mathrm{v}})} \sim \exp(-\hbar\omega_{\mathrm{v}}/kT) \tag{29}$$

for any frequency shift $\Delta\omega$. We use $n_{\mathrm{v}} = [\exp(\hbar\omega_{\mathrm{v}}/T) - 1]^{-1}$ in the last step in Eq. (29). Thus, as it takes place in Raman scattering, the intensity of the anti-Stokes component is inhibited compared with the intensity of the Stokes component by the factor $\exp(-\hbar\omega_{\mathrm{v}}/kT)$.

IV. STATISTICAL PROPERTIES OF SCATTERED LIGHT

We now consider the question of how the statistical properties of thermal vibrations of the nuclei of a molecule and the statistical properties of an external light source manifest themselves in the statistical properties of Stokes and anti-Stokes light. The interaction between TLS and free space modes leads to the energy dissipation through the radiation emission. To find the irradiated electric field, we obtain the equations on the field amplitude of the free space mode $\hat{a}_{\mathbf{k},\mu}$ that follows from the Hamiltonians (4), (5)

$$\frac{d\hat{a}_{\mathbf{k},\mu}}{dt} = -i\omega_{\mathbf{k}}\hat{a}_{\mathbf{k},\mu} - i\frac{\boldsymbol{E}_{\mathbf{k},\mu}\cdot\boldsymbol{d}_{\mathrm{eg}}}{\hbar}\hat{\sigma}(t). \tag{30}$$

The solution of the Eq. (30) is

$$\hat{a}_{\mathbf{k},\mu}(t) = \hat{a}_{\mathbf{k},\mu}(0)\exp(-i\omega_{\mathbf{k}}t) - i\frac{\boldsymbol{E}_{\mathbf{k},\mu}\cdot\boldsymbol{d}_{\mathrm{eg}}}{\hbar} \times \int_0^t dt'\hat{\sigma}(t')e^{-i\omega_{\mathbf{k}}(t-t')}. \tag{31}$$

The first part represents the vacuum field amplitude while the second one corresponds to the field irradiated by the molecule.

We are interested not in the separate amplitude $\hat{a}_{\mathbf{k},\mu}$, but in the *total* electric field, $\hat{\boldsymbol{E}}(\mathbf{r},t) = \sum_{\mathbf{k},\mu}\boldsymbol{E}_{\mathbf{k},\mu}\hat{a}_{\mathbf{k},\mu}(t)$, irradiated by the molecule, detected by the detector located at point $\mathbf{r}$ [65]. To calculate this total electric field, we assume that the molecule is at the point $\mathbf{r} = 0$ and use Eq. (31). As a result, we obtain

$$\hat{\boldsymbol{E}}(\mathbf{r},t) = \sum_{\mathbf{k},\mu}\boldsymbol{E}_{\mathbf{k},\mu}\hat{a}_{\mathbf{k},\mu}(0)\exp(-i\omega_{\mathbf{k}}t) + \hat{\boldsymbol{E}}_{\mathrm{R}}(\mathbf{r},t) + \hat{\boldsymbol{E}}_{\mathrm{St}}(\mathbf{r},t) + \hat{\boldsymbol{E}}_{\mathrm{aSt}}(\mathbf{r},t), \tag{32}$$

where the Rayleigh, $\hat{\boldsymbol{E}}_{\mathrm{R}}(\mathbf{r},t)$, Stokes, $\hat{\boldsymbol{E}}_{\mathrm{St}}(\mathbf{r},t)$, and anti-Stokes, $\hat{\boldsymbol{E}}_{\mathrm{aSt}}(\mathbf{r},t)$, components of the scattered electric field are given by

$$\hat{\boldsymbol{E}}_j(\mathbf{r},t) = \sum_{\mathbf{k},\mu}\boldsymbol{E}_{\mathbf{k},\mu}(\boldsymbol{E}_{\mathbf{k},\mu}\cdot\boldsymbol{d}_{\mathrm{eg}}/\hbar)e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\omega_j t} \times \int_0^t dt'[\hat{\sigma}_j(t')e^{i\omega_j t'}]e^{i(\omega_{\mathbf{k}}-\omega_j)(t'-t)}, \tag{33}$$

where $j = \mathrm{R}$, St, aSt and $\omega_{\mathrm{R}} = \omega_\Omega$. We assume that the detectors for Rayleigh, Stokes, and anti-Stokes, scattered field are placed at $\mathbf{r}_{\mathrm{R}}$, $\mathbf{r}_{\mathrm{St}}$, and $\mathbf{r}_{\mathrm{aSt}}$, such that $|\mathbf{r}_{\mathrm{R}}| = |\mathbf{r}_{\mathrm{St}}| = |\mathbf{r}_{\mathrm{aSt}}| = r$. We also assume that the detectors are not polarization sensitive. Summation in (33) can be performed by using density of vacuum EM field states: $\sum_{\mathbf{k}} \rightarrow$

$V(2\pi)^{-3}c^{-3}\int_0^{+\infty} d\omega\omega^2 \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\varphi$. Integration over ω of the fast oscillating function $e^{i(\omega_{\mathbf{k}}-\omega_j)(t-t')}$ in expressions for $\hat{E}_{\rm R}(t)$, $\hat{E}_{\rm St}(t)$, and $\hat{E}_{\rm aSt}(t)$ gives (for details of calculations see [65])

$$\hat{E}_j(t) \propto \hat{\sigma}_j(t - r/c), \tag{34}$$

where $j = {\rm R, St, aSt}$. Using the connection between the operators of the molecular dipole moment and the field amplitude, Eq. (34), one can express the second-order autocorrelation function of scattered light as

$$\begin{aligned} g^{(2)}_{j,j}(\tau) &= \frac{\langle \hat{E}_j^\dagger(t)\hat{E}_j^\dagger(t+\tau)\hat{E}_j(t+\tau)\hat{E}_j(t)\rangle}{\langle \hat{E}_j^\dagger(t)\hat{E}_j(t)\rangle\langle \hat{E}_j^\dagger(t+\tau)\hat{E}_j(t+\tau)\rangle} \\ &= \frac{\langle \hat{\sigma}_j^\dagger(t_r)\hat{\sigma}_j^\dagger(t_r+\tau)\hat{\sigma}_j(t_r+\tau)\hat{\sigma}_j(t_r)\rangle}{\langle \hat{\sigma}_j^\dagger(t_r)\hat{\sigma}_j(t_r)\rangle\langle \hat{\sigma}_j^\dagger(t_r+\tau)\hat{\sigma}_j(t_r+\tau)\rangle}, \end{aligned} \tag{35}$$

where $j = {\rm R, St, aSt}$ and $t_r = t - r/c$. Substituting the dipole moment operators of the molecule (16)–(18) into the expression for the autocorrelation function (35) and using the correlations (11), (12) and (2), (3), we obtain

$$g^{(2)}_{R,R}(\tau) = g^{(2)}_{\Omega}(\tau), \tag{36}$$

$$g^{(2)}_{\rm St,St}(\tau) = g^{(2)}_{\Omega}(\tau) \times g^{(2)}_{\rm v}(\tau), \tag{37}$$

$$g^{(2)}_{\rm aSt,aSt}(\tau) = g^{(2)}_{\Omega}(\tau) \times g^{(2)}_{\rm v}(\tau). \tag{38}$$

Thus, the statistical properties of Rayleigh scattered light are determined only by the statistical properties of an external source. In particular, in the case of ideally coherent field, $g^{(2)}_{\Omega}(\tau) = 1$, the Rayleigh scattered light has $g^{(2)}_{R,R}(\tau) = 1$ which is confirmed by the previous theoretical result [68]. At the same time, the statistical properties of Stokes and anti-Stokes scattered light are determined by both the statistical properties of an external source and the statistical properties of thermal vibrations of the nuclei of a molecule.

We note that the value of the second-order coherence function strongly depends on the width of the filter frequency region, which cuts off from the scattered signal. This problem recently has attracted considerable attention [68,69]. Moreover, in the paper [68] it was shown that, in nonresonant scattering of coherent light on a TLS, filtering all the scattered spectrum except for Rayleigh signal leads to unity autocorrelation function. Expression (36) is consistent with this result.

The second-order autocorrelation function $g^{(2)}_{\rm v}(\tau)$ of the vibrations of the nuclei of the molecule can be found by substituting Eq. (19) to the general expression for $g^{(2)}_{\rm v}(\tau)$:

$$g^{(2)}_{\rm v}(\tau) = \frac{\langle \hat{b}^\dagger_{\rm th}(t)\hat{b}^\dagger_{\rm th}(t+\tau)\hat{b}_{\rm th}(t+\tau)\hat{b}_{\rm th}(t)\rangle}{\langle \hat{b}^\dagger_{\rm th}(t)\hat{b}_{\rm th}(t)\rangle\langle \hat{b}^\dagger_{\rm th}(t+\tau)\hat{b}_{\rm th}(t+\tau)\rangle}. \tag{39}$$

Using Eqs. (9)–(12), we obtain

$$g^{(2)}_{\rm v}(\tau) = 1 + e^{-2\gamma_{\rm v}|\tau|}. \tag{40}$$

Note that in the case of a coherent external source $g^{(2)}_{\Omega}(\tau) = 1$ the autocorrelation function of Rayleigh scattered light coincides with the autocorrelation function of coherent light, $g^{(2)}_{R,R}(\tau) = 1$, and the autocorrelation functions of Stokes and anti-Stokes light at $\tau = 0$ are equal to the autocorrelation function of a thermal light, $g^{(2)}_{\rm St,St}(0) = 2$ and $g^{(2)}_{\rm aSt,aSt}(0) = 2$, and tend to unity with characteristic time $\gamma_{\rm v}^{-1}$.

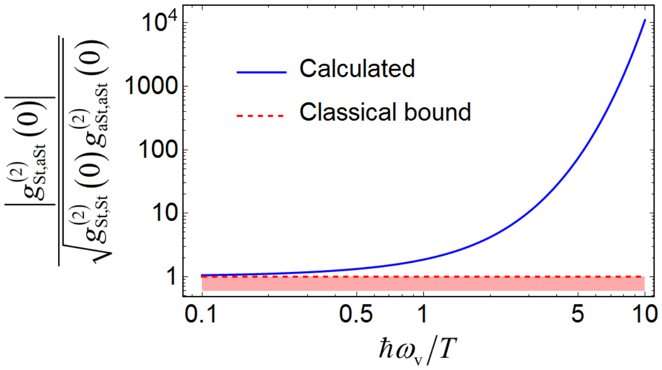

FIG. 1. The cross-correlation function of the second order of the Stokes and anti-Stokes signals referred to the autocorrelation functions of the second order of these signals, depending on the ratio of the vibration frequency of the nuclei of the molecule to the ambient temperature of the molecule. The blue solid curve is the cross-correlation function calculated by Eq. (42), the red dashed line is the classic restriction for this quantity. The red shaded area is the classically allowed range of values for the cross-second-order autocorrelation function of the Stokes and anti-Stokes lights.

We now consider the question of how the statistical properties of an external source (3) and the statistical properties of thermal vibrations of the nuclei of molecules (40) affect the cross correlations between Stokes and anti-Stokes scattered light. Cross correlations between Stokes and anti-Stokes light will be characterized by a second-order cross-correlation function [4,32],

$$\begin{aligned} g^{(2)}_{\rm St,aSt}(\tau) &= \frac{\langle \hat{E}^\dagger_{\rm St}(t)\hat{E}^\dagger_{\rm aSt}(t+\tau)\hat{E}_{\rm aSt}(t+\tau)\hat{E}_{\rm St}(t)\rangle}{\langle \hat{E}^\dagger_{\rm St}(t)\hat{E}_{\rm St}(t)\rangle\langle \hat{E}^\dagger_{\rm aSt}(t+\tau)\hat{E}_{\rm aSt}(t+\tau)\rangle} \\ &= \frac{\langle \hat{\sigma}^\dagger_{\rm St}(t_r)\hat{\sigma}^\dagger_{\rm aSt}(t_r+\tau)\hat{\sigma}_{\rm aSt}(t_r+\tau)\hat{\sigma}_{\rm St}(t_r)\rangle}{\langle \hat{\sigma}^\dagger_{\rm St}(t_r)\hat{\sigma}_{\rm St}(t_r)\rangle\langle \hat{\sigma}^\dagger_{\rm aSt}(t_r+\tau)\hat{\sigma}_{\rm aSt}(t_r+\tau)\rangle}. \end{aligned} \tag{41}$$

Substituting the dipole moment operators of the molecule (17), (18) into the expression for the second-order cross-correlation function (41) and using the correlations (11), (12) and (2), (3) we obtain

$$g^{(2)}_{\rm St,aSt}(\tau) = g^{(2)}_{\Omega}(\tau) \times \left(1 + \frac{1+n_{\rm v}}{n_{\rm v}} e^{-2\gamma_{\rm v}|\tau|}\right). \tag{42}$$

It follows from this relation that the second-order cross-correlation function for Stokes and anti-Stokes light is determined by both the statistical properties of the external source $g^{(2)}_{\Omega}(\tau)$ and the average number of vibrational quanta of the nuclei of the molecule $n_{\rm v}$ under the influence of thermal fluctuations of the environment.

The classical restriction of the magnitude of the cross-correlation function of the second order (42) can be written in the form of inequality $|g^{(2)}_{\rm St,aSt}(0)| \leqslant \sqrt{g^{(2)}_{\rm St,St}(0) g^{(2)}_{\rm aSt,aSt}(0)}$ [4]. Figure 1 shows the ratio $|g^{(2)}_{\rm St,aSt}(0)|/\sqrt{g^{(2)}_{\rm St,St}(0) g^{(2)}_{\rm aSt,aSt}(0)}$ as a function of the ratio the vibration frequency of the nuclei of the molecule to the ambient temperature of the molecule, $\hbar\omega_{\rm v}/T$. It is seen that the cross-correlation function of the

Stokes and anti-Stokes scattered light exceeds the classical limit for any relations between the oscillation frequency ω_v and temperature T. Note that from expressions (37), (38) and (42) it follows that the ratio $|g^{(2)}_{\mathrm{St,aSt}}(0)|/\sqrt{g^{(2)}_{\mathrm{St,St}}(0)g^{(2)}_{\mathrm{aSt,aSt}}(0)}$ does not depend on the statistics of an external source $\hat{\Omega}(t)$. In this sense, the statistics of an external source does not change the "nonclassicality" of the correlations between the Stokes and anti-Stokes light. In Appendix B, we also examine the question of the cross correlation of Stokes photons and vibrations of the nuclei of a molecule.

V. PROBABILITY OF SIMULTANEOUS DETECTION OF STOKES AND ANTI-STOKES PHOTONS

As we showed in the previous section, the statistics of an external source do not affect the fulfillment of the criterion for the classicality of cross correlations $|g^{(2)}_{\mathrm{St,aSt}}(0)| \leqslant \sqrt{g^{(2)}_{\mathrm{St,St}}(0)g^{(2)}_{\mathrm{aSt,aSt}}(0)}$, nevertheless, the statistics of an external field does affect the magnitude of the second-order cross-correlation function $g^{(2)}_{\mathrm{St,aSt}}(\tau)$. As mentioned in the Introduction, in some applications this characteristic is important on its own, e.g., it may improve the properties of heralded photon sources. Below we consider this question in more detail.

The probability of detecting a Stokes photon at time $t+\tau$ at detector 2 provided that the anti-Stokes photon was detected at time t at detector 1 is related to the value of the second-order cross-correlation function $g^{(2)}_{\mathrm{St,aSt}}(\tau)$ [7,25] as follows. If we designate $\Phi_{\mathrm{aSt}}(t)$ the event at which the anti-Stokes photon is detected on the first detector from the moment of time t, and $\Phi_{\mathrm{St}}(t+\tau)$ the event at which the Stokes photon is detected at the second detector at the time $t+\tau$, then we can write the relation [7,25]

$$P[\Phi_{\mathrm{St}}(t+\tau)|\Phi_{\mathrm{aSt}}(t)] = g^{(2)}_{\mathrm{St,aSt}}(\tau)P[\Phi_{\mathrm{St}}(t+\tau)], \tag{43}$$

where $P[\Phi_{\mathrm{St}}(t+\tau)|\Phi_{\mathrm{aSt}}(t)]$ is the probability of the event $\Phi_{\mathrm{St}}(t+\tau)$ provided that the $\Phi_{\mathrm{aSt}}(t+\tau)$ has occurred, $P[\Phi_{\mathrm{St}}(t+\tau)]$ is the probability of the event $\Phi_{\mathrm{St}}(t+\tau)$, and $g^{(2)}_{\mathrm{St,aSt}}(\tau)$ is the cross-correlation function of the second order for the Stokes and anti-Stokes signals, defined by expression (41). Thus, a large value $g^{(2)}_{\mathrm{St,aSt}}(\tau)$ increases the probability of the simultaneous arrival of Stokes and anti-Stokes photons at the first and second detectors.

The obtained expressions (42) and (43) show how one can improve the properties of the heralded light source based on the spontaneous Raman scattering with an external light source. The first way to improve the properties of the heralded light source based on the spontaneous Raman scattering is the use of an external source with a large autocorrelation function $g^{(2)}_{\Omega}(0)$. Indeed, according to expression (42) an increase in the autocorrelation function of the second order of the external source $g^{(2)}_{\Omega}(0)$ leads to an increase in cross correlations between Stokes and anti-Stokes light $g^{(2)}_{\mathrm{St,aSt}}(0) \propto g^{(2)}_{\Omega}(0)$. This, in turn, according to expression (43), leads to an increase in the probability of detecting a Stokes photon $P[\Phi_{\mathrm{aSt}}(t)|\Phi_{\mathrm{St}}(t)]$ at the time of detection of an anti-Stokes photon. For example, *ceteris paribus*, the relation between probability $P_{\mathrm{coh}}[\Phi_{\mathrm{aSt}}(t)|\Phi_{\mathrm{St}}(t)]$ when using a coherent light source with $g^{(2)}_{\Omega}(0) = 1$ and probability when using a light source with an autocorrelation function $g^{(2)}_{\Omega}(0) > 1$ is equal to

$$P[\Phi_{\mathrm{St}}(t)|\Phi_{\mathrm{aSt}}(t)] = g^{(2)}_{\Omega}(0)P_{\mathrm{coh}}[\Phi_{\mathrm{St}}(t)|\Phi_{\mathrm{aSt}}(t)]. \tag{44}$$

That is, the probability $P[\Phi_{\mathrm{St}}(t)|\Phi_{\mathrm{aSt}}(t)]$ increases by a factor of $g^{(2)}_{\Omega}(0)$ compared with the probability $P_{\mathrm{coh}}[\Phi_{\mathrm{St}}(t)|\Phi_{\mathrm{aSt}}(t)]$.

The second way to improve the properties of the heralded light source based on the spontaneous Raman scattering is to use a source with the autocorrelation function rapidly decreasing over time $g^{(2)}_{\Omega}(\tau)$. According to the expressions (42) and (3) at the initial instant of time, the cross correlations between Stokes and anti-Stokes light $g^{(2)}_{\mathrm{St,aSt}}(\tau)$ decrease for large $g^{(2)}_{\Omega}(0)$ and small n_v approximately as

$$g^{(2)}_{\mathrm{St,aSt}}(\tau) \approx \frac{g^{(2)}_{\Omega}(0)}{n_v} e^{-(\Gamma_2+2\gamma_v)|\tau|}. \tag{45}$$

Thus, according to (45) and (43) we can obtain

$$P[\Phi_{\mathrm{St}}(t+\tau)|\Phi_{\mathrm{aSt}}(t)] \approx P[\Phi_{\mathrm{St}}(t)|\Phi_{\mathrm{aSt}}(t)]e^{-(\Gamma_2+2\gamma_v)|\tau|}. \tag{46}$$

In other words, by increasing the decay rate of the second-order autocorrelation function Γ_2 one can increase the "simultaneity" of the radiation of Stokes and anti-Stokes photons. This may reduce the accidental coincidence rate that originates from uncorrelated photons [12]. Usage of the photon pair sources with fast decaying probability $P[\Phi_{\mathrm{St}}(t+\tau)|\Phi_{\mathrm{aSt}}(t)]$ suppresses the photons and noise counts [70].

VI. DISCUSSION AND CONCLUSION

In this work, we examined the statistical properties of Raman radiation upon scattering by thermalized phonons. We obtained analytical expression (42) for the second-order cross-correlation function of the Stokes and anti-Stokes scattered radiation $g^{(2)}_{\mathrm{St,aSt}}(\tau)$. An analysis of this expression shows that the intensity cross correlations of the Stokes and anti-Stokes radiation during scattering by thermal phonons always have a nonclassical character, which manifests itself in the fulfillment of the inequality $|g^{(2)}_{\mathrm{St,aSt}}(0)| > \sqrt{g^{(2)}_{\mathrm{St,St}}(0)g^{(2)}_{\mathrm{aSt,aSt}}(0)}$. The higher the ratio of the natural frequency of nuclear vibrations to temperature the greater the ratio $|g^{(2)}_{\mathrm{St,aSt}}(0)|/\sqrt{g^{(2)}_{\mathrm{St,St}}(0)g^{(2)}_{\mathrm{aSt,aSt}}(0)}$.

The experimental values for the second-order correlation function of the Stokes and anti-Stokes scattered light [6–8,12–14,17] turn out to be lower than those calculated by the formula (42). This is due to the presence of spurious signals at the Stokes and anti-Stokes scattering frequencies from the external pump, as well as the fact that the high intensity of an external source can lead to the removal of phonons from the thermal state. Therefore, expression (42) should be considered as the upper limit for the second-order correlation function of the Stokes and anti-Stokes scattered light.

Note that a large value $g^{(2)}_{\mathrm{St,aSt}}(0)$ can be used to improve the properties of single-photon sources. For example, in the scheme of a conventional single-photon source, presented, for example, in [33], the second-order autocorrelation function $g^2(0)$ is approximately equal to $g^{(2)}_{\mathrm{cond}}(0) \approx g^{(2)}_{\mathrm{St,St}}(0) g^{(2)}_{\mathrm{aSt,aSt}}(0)/g^{(2)}_{\mathrm{aSt,St}}(0)$ [33]. Thus, from (42) we obtain that $g^{(2)}_{\mathrm{cond}}(0) \approx 4 g^{(2)}_{\Omega}(0) n_{\mathrm{v}}/(1+2n_{\mathrm{v}})$, and for $n_{\mathrm{v}} \ll 1$ one can obtain conditional single-photon sources with a low autocorrelation function $g^{(2)}_{\mathrm{cond}}(0)$.

From the expression for the second-order correlation function of the Stokes and anti-Stokes scattered light, the following estimation takes place: $g^{(2)}_{\mathrm{St,aSt}}(0) \sim 1/n_{\mathrm{v}}$. A similar estimate for the value $g^{(2)}_{\mathrm{St,aSt}}(0)$ was previously obtained in [14] from an analysis of the probabilities of detecting Stokes and anti-Stokes photons. Computer modeling of the second-order correlation function of the Stokes and anti-Stokes scattered light was also carried out in [12–14,71] based on the solution of the Lindblad equation.

In this work, we considered the possibility of controlling the second-order correlation function of the Stokes and anti-Stokes scattered light $g^{(2)}_{\mathrm{St,aSt}}(\tau)$ using the photon statistics of an external light source. We have shown that an increase in the second-order autocorrelation function of an incident light source $g^{(2)}_{\Omega}(0)$ leads to an increase in the correlations between Stokes and anti-Stokes light $g^{(2)}_{\mathrm{St,aSt}}(0)$. The results presented in this work may be useful for improving the properties of sources of paired photons based on spontaneous Raman scattering.

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APPENDIX A: SOLUTION OF THE EQUATIONS (6), (7) IN PERTURBATION THEORY

In this appendix we construct a solution to the operator system of equations (6),(7) using perturbation theory with the two small parameters $\varepsilon_1 = \sqrt{I}/|\omega_\Omega - \omega_0|$ and $\varepsilon_2 = g/|\omega_\Omega - \omega_0|$. In each order of perturbation theory, we obtain the exactly solvable linear system of operator equation with quantum noise. In the first order of perturbation theory we obtain Rayleigh response on the frequency of the external field ω_Ω. The higher orders of the perturbation theory describe the response of the system on the side frequencies.

In the zeroth order of perturbation theory, the system of equations (6), (7) takes the form

$$d\hat{b}_0/dt + (i\omega_{\mathrm{v}} + \gamma_{\mathrm{v}})\hat{b}_0 = \hat{F}_b(t), \tag{A1}$$

$$d\hat{\sigma}_0/dt + (i\omega_0 + \gamma_\perp)\hat{\sigma}_0 = 0. \tag{A2}$$

The solution to the system of equations (A1), (A2) at times $t \gg \gamma_\perp^{-1}, \gamma_{\mathrm{v}}^{-1}$ has the form

$$\hat{b}_0(t) = \int_0^t G_b(t-t')\hat{F}_b(t')dt', \tag{A3}$$

$$\hat{\sigma}_0 = 0. \tag{A4}$$

In the first order of perturbation theory, the system of equations (6), (7) takes the form

$$d\hat{b}_1/dt + (i\omega_{\mathrm{v}} + \gamma_{\mathrm{v}})\hat{b}_1 = 0, \tag{A5}$$

$$d\hat{\sigma}_1/dt + (i\omega_0 + \gamma_\perp)\hat{\sigma}_1 = -i\hat{\Omega}(t)e^{-i\omega_\Omega t}. \tag{A6}$$

The solution to the system of equations (A5), (A6) at times $t \gg \gamma_\perp^{-1}, \gamma_{\mathrm{v}}^{-1}$ has the form

$$\hat{b}_1 = 0, \tag{A7}$$

$$\hat{\sigma}_1(t) = \frac{\hat{\Omega}(t)}{\omega_\Omega - \omega_0}e^{-i\omega_\Omega t}. \tag{A8}$$

The solution (A8) is a driven solution; the dipole moment follows the external electric field oscillating with its frequency ω_Ω.

In the second order of perturbation theory, Eq. (6) takes the form

$$d\hat{\sigma}_2/dt + (i\omega_0 + \gamma_\perp)\hat{\sigma}_2 = -ig\hat{\sigma}_1(t)\big(\hat{b}_0^\dagger(t) + \hat{b}_0(t)\big). \tag{A9}$$

We use that $\hat{\sigma}_1(t) \propto e^{-i\omega_\Omega t}$ and $\hat{b}_0(t) \propto e^{-i\omega_{\mathrm{v}} t}$, then the solution of Eq. (A9) can be approximately written in the form

$$\hat{\sigma}_2(t) = \frac{g}{\omega_\Omega + \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_1(t)\hat{b}_0(t) + \frac{g}{\omega_\Omega - \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_1(t)\hat{b}_0^\dagger(t). \tag{A10}$$

The first term of the right-hand side of Eq. (A10) oscillates with the frequency $\omega_{\mathrm{aSt}} = \omega_\Omega + \omega_{\mathrm{v}}$ and the second term oscillates with the frequency $\omega_{\mathrm{St}} = \omega_\Omega - \omega_{\mathrm{v}}$. The emerging of the new frequencies ω_{aSt} and ω_{St} is due to the nonlinear process: the oscillations of the nuclei in the molecule modulate the induced electronic dipole moment of the molecule. The frequency of the nuclei oscillations ω_{v} determines the shift of the side frequencies with respect to the frequency of the incident light ω_Ω.

Thus, the solution for the electronic dipole moment of the molecule in the first nonvanishing order in the small parameters ε_1 and ε_2 has the form $\hat{\sigma}(t) \approx \hat{\sigma}_0(t) + \hat{\sigma}_1(t) + \hat{\sigma}_2(t)$,

$$\begin{aligned}\hat{\sigma}(t) = {}& \frac{\hat{\Omega}(t)}{\omega_\Omega - \omega_0}e^{-i\omega_\Omega t} + \frac{g}{\omega_\Omega - \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_1(t)\hat{b}_0^\dagger(t) \\ &+ \frac{g}{\omega_\Omega + \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_1(t)\hat{b}_0(t).\end{aligned} \tag{A11}$$

We denote

$$\hat{\sigma}_{\mathrm{R}}(t) = \frac{\hat{\Omega}(t)}{\omega_\Omega - \omega_0}e^{-i\omega_\Omega t}, \tag{A12}$$

$$\hat{b}_{\mathrm{th}}(t) = \hat{b}_0(t) = \int_0^t G_b(t-t')\hat{F}_b(t')dt', \tag{A13}$$

$$\hat{\sigma}_{\mathrm{St}}(t) = \frac{g}{\omega_\Omega - \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_{\mathrm{R}}(t)\hat{b}_{\mathrm{th}}^\dagger(t), \tag{A14}$$

$$\hat{\sigma}_{\mathrm{aSt}}(t) = \frac{g}{\omega_\Omega + \omega_{\mathrm{v}} - \omega_0}\hat{\sigma}_{\mathrm{R}}(t)\hat{b}_{\mathrm{th}}(t), \tag{A15}$$

and arrive at expression (15).

APPENDIX B: CORRELATIONS BETWEEN STOKES SCATTERED LIGHT AND VIBRATIONS OF MOLECULAR NUCLEI

In this appendix, we will consider the question of the correlation of Stokes scattered light and vibrations of the nuclei of a molecule. Interest in these correlations arose in connection with a recent experiment [23], where nonclassical correlations between Stokes light and phonons were demonstrated during Raman scattering in a silicon waveguide.

The cross-correlation function of the Stokes light and the vibrations of the nuclei of molecules $g^{(2)}_{\mathrm{St,v}}(\tau)$ can be determined by analogy with the expression (41)

$$g^{(2)}_{\mathrm{St,v}}(\tau) = \frac{\langle \hat{E}^{\dagger}_{\mathrm{St}}(t)\hat{b}^{\dagger}_{\mathrm{th}}(t_r+\tau)\hat{b}_{\mathrm{th}}(t_r+\tau)\hat{E}_{\mathrm{St}}(t)\rangle}{\langle \hat{E}^{\dagger}_{\mathrm{St}}(t)\hat{E}_{\mathrm{St}}(t)\rangle\langle \hat{b}^{\dagger}_{\mathrm{th}}(t_r+\tau)\hat{b}_{\mathrm{th}}(t_r+\tau)\rangle}$$
$$= \frac{\langle \hat{\sigma}^{\dagger}_{\mathrm{St}}(t_r)\hat{b}^{\dagger}_{\mathrm{th}}(t+\tau)\hat{b}_{\mathrm{th}}(t_r+\tau)\hat{\sigma}_{\mathrm{St}}(t_r)\rangle}{\langle \hat{\sigma}^{\dagger}_{\mathrm{St}}(t_r)\hat{\sigma}_{\mathrm{St}}(t_r)\rangle\langle \hat{b}^{\dagger}_{\mathrm{th}}(t_r+\tau)\hat{b}_{\mathrm{th}}(t_r+\tau)\rangle}, \quad \text{(B1)}$$

where $t_r = t - r/c$ and r is the distance between the emitter of the Stokes light and the detector. Here we used the proportionality of the operator of the amplitude of the Stokes radiation and the operator of the corresponding component of the dipole moment of the molecule (34). Substitution of expression (17) into (B1) leads to

$$g^{(2)}_{\mathrm{St,v}}(\tau) = 1 + \frac{1+n_{\mathrm{v}}}{n_{\mathrm{v}}}e^{-2\gamma_{\mathrm{v}}|\tau|}. \quad \text{(B2)}$$

Expression (B2) up to the autocorrelation function of an external source $g^{(2)}_{\Omega}(\tau)$ coincides with expression (42) for the cross-correlation function of the second order of Stokes and anti-Stokes light $g^{(2)}_{\mathrm{St,aSt}}(\tau)$. As a consequence, all arguments about the nonclassical character of the correlation function $g^{(2)}_{\mathrm{St,aSt}}(\tau)$ remain valid for the quantity $g^{(2)}_{\mathrm{St,v}}(\tau)$. This conclusion is in agreement with the experiment from the work [23] where nonclassical correlations between the phonons and Stokes photons have been demonstrated.

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