Power dependence of Klyshko’s Stokes-anti-Stokes correlation in the inelastic scattering of light

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Abstract

The Stokes and anti-Stokes components in the inelastic scattering of light are related to phonon statistics and have been broadly used to measure temperature and phonon lifetimes in different materials. However, correlation between the components are expected to change the Stokes/anti-Stokes intensity ratio, imposing corrections to the broadly used Bose-Einstein boson statistics. Here the excitation power dependence of these scattering processes is theoretically described by an effective Hamiltonian that includes correlation between the Stokes and the anti-Stokes events. The model is used to fit available experimental results in three-dimensional diamond and two-dimensional graphene, showing that the phenomena can dramatically increase in the low-dimensional system under specific resonance conditions. This work shows that the Stokes-anti-Stokes correlation has to be considered when using Raman spectroscopy to extract phonon-dependent structural and transport properties of low-dimensional structures, and that graphene can become a new source for correlated photons in quantum optics and information processing.

KEYWORDS: light scattering, diamond, graphene, Stokes-anti-Stokes correlation

PACS numbers:
The inelastic scattering of light by matter [1] exhibits two components: the *Stokes* \( (S) \), where an incident photon is converted into a phonon and a red-shifted \( S \) photon, and the *anti-Stokes* \( (aS) \), where one incident photon and one existing phonon are annihilated, generating a blue-shifted \( aS \) photon. The Stokes/anti-Stokes intensity ratio is a signature of the quantum character of lattice vibrations, considered to be defined by the Bose-Einstein distribution for bosons

\[
\frac{I_{aS}}{I_S} = C \frac{n_0}{1 + n_0},
\]

where \( C \) depends on the optical setup, and \( n_0 = (e^{\hbar \nu / k_B T} - 1)^{-1} \) is the effective phonon population [2]. \( n_0 \ll 1 \) for phonons with energies \( \hbar \nu \) larger than the thermal energy \( k_B T \) \((k_B \) is the Boltzman constant). The \( I_{aS}/I_S \) intensity ratio is used to measure phonon lifetimes [3], local effective temperatures [4, 5] and optical resonances [6], and except for very specific resonance conditions, the \( I_{aS}/I_S \) ratio should approach the unit only if the temperature is high enough to activate a very large phonon population. However, Klyshko [7, 8] has proposed a correlated process, called here the *Stokes-anti-Stokes* \( (SaS) \) event, where a phonon created by the Stokes process is subsequently annihilated in the anti-Stokes process. If the \( SaS \) event is significant, the picture described by the Bose-Einstein phonon distribution is not complete, and Eq.1 has to be generalized.

Evidences for the \( SaS \) process are accumulating in material science [3, 5, 9–11], generating interests in quantum optics [9, 11]. Lee et al. [9] demonstrated the quantum nature of the \( SaS \) correlation in diamond by measuring a non-classical \( SaS \) field correlation function \( g^{(2)} \). Klyshko [8] pointed that the correlated character of this \( S \) and \( aS \) photons can be continuously varied from purely quantum to purely classical and Kasperczyk et al. [11] explored this transition in character by changing the photon and phonon reservoirs through changes in the excitation laser power. While these experiments are usually performed with ultra-fast pulsed lasers to enhance the response of the non-linear \( SaS \) event, Jorio et al. [10] have provided evidences for the observation of dominant \( SaS \) event using a few miliwatts continuum wave (CW) laser, i.e. achievable even with a simple laser pointer. This result was obtained in twisted-bilayer graphene (tBLG), a two-dimensional system specially engineered to exhibit resonance with the \( aS \) photon emission [10]. Since phonons have a significant lifetime, it has been proposed that these systems can work as a solid state quantum memory, storing information between the write (*Stokes*) and read (*anti-Stokes*) processes [9]. In diamond and graphene \( \hbar \nu \gg k_B T \), and the quantum memory works at room temperature.
Here the $I_{as}/I_S$-based phonon population analysis is generalized by proposing an effective Hamiltonian that explicitly considers the Stokes and anti-Stokes fields correlation, on a simple formalism that is able to fit the experimental results from diamond and graphene. The Hamiltonian is given by

$$\hat{H} = \omega_0 \hat{a}^\dagger \hat{a} + \nu \hat{c}^\dagger \hat{c} + \omega_S \hat{b}_S^\dagger \hat{b}_S + \omega_{as} \hat{b}_{as}^\dagger \hat{b}_{as}$$

$$+ \lambda_S (\hat{a} \hat{c}^\dagger \hat{b}_S^\dagger + \text{h.c.}) + \lambda_{as} (\hat{a} \hat{c} \hat{b}_{as}^\dagger + \text{h.c.}),$$

(2)

where $\hat{b}_{S,as}$ ($\hat{b}_{S,as}^\dagger$), $\hat{c}$ ($\hat{c}^\dagger$) and $\hat{a}$ ($\hat{a}^\dagger$) represent the annihilation (creation) operator of Stokes ($S$), anti-Stokes ($as$), phonon ($c$) and incident ($a$) fields respectively. $\lambda_S$ and $\lambda_{as}$ are the coupling constants. The $\lambda_S$ coupling term describes the creation of an $S$ photon and a phonon through the absorption of an incident photon, and the $\lambda_{as}$ term describes the creation of an $as$ photon through the absorption of an incident photon and a phonon. All energies are measured in units of frequencies by setting $\hbar = 1$. $\omega_0$ and $\nu$ are the incident and the phonon fields energies, respectively, then the Stokes and anti-Stokes modes have energies given by $\omega_{aS,S} = \omega_0 \pm \nu$. Typically, the coherent sources used in experiments of this type can be considered to have large enough number of photons, which allows us to replace $(\hat{a}, \hat{a}^\dagger) \rightarrow |\alpha\rangle$, with $|\alpha|^2$ being the mean number of incident photons. The laser power is given by $P_L = \mathcal{A} |\alpha|^2$, $\mathcal{A}$ being a constant depending on the laser energy. The Hamiltonian model above is valid within the coherence time of the pumping laser, whether continuum or pulsed.

Hamiltonian (2) accounts for the interaction at the material but it does not properly describe the dissipation of the created excitations due to the presence of the photonics and phononic reservoirs. Such dynamics can be computed by means of the Markovian master equation [12] for the overall reduced density operator of the three fields, introducing decay rates of phonons and scattered photons. The master equation for the density operator $\dot{\hat{\rho}} = \text{Tr}_R \hat{\rho}_{\text{total}}$, in the Lindblad form reads

$$\frac{d}{dt} \hat{\rho} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}(\hat{\rho}),$$

(3)

where $\text{Tr}_R$ indicates the tracing out of the reservoir degrees of freedom. The Lindbladian
term in our model is $\mathcal{L} = \mathcal{L}_b + \mathcal{L}_c$, with:

$$
\mathcal{L}_b(\dot{\rho}) = -\sum_{x=S,aS} \gamma_x (\dot{b}_x^\dagger \hat{b}_x + \dot{\rho} \hat{b}_x^\dagger \hat{b}_x - 2\hat{b}_x \hat{b}_x^\dagger \dot{\rho})
$$

$$
\mathcal{L}_c(\dot{\rho}) = -\gamma_c (n_0 + 1)(\dot{c}^\dagger \hat{c} \dot{\rho} + \dot{\rho} \hat{c}^\dagger \hat{c}^\dagger - 2\hat{c}^\dagger \hat{c} \dot{\rho})
$$

$$
-\gamma_c n_0 (\dot{\hat{c}}^\dagger \hat{c} + \dot{\rho} \hat{c}^\dagger \hat{c}^\dagger - 2\hat{c}^\dagger \hat{c} \dot{\rho}),
$$

(4)

with $\gamma_s$, $\gamma_{as}$ and $\gamma_c$ being the decay rates (proportional to the inverse of the coherence time) of the respective Stokes, anti-Stokes and phonon fields. To analyze the Stokes and anti-Stokes field intensities and their respective correlation function at zero delay ($\tau = 0$), we compute the average values

$$
\langle n_{S,aS} \rangle = \langle \hat{b}_{S,aS}^\dagger \hat{b}_{S,aS} \rangle, \quad \langle n_c \rangle = \langle \hat{c}^\dagger \hat{c} \rangle, \quad g^2(0) = \frac{\langle \hat{b}_{S,aS}^\dagger \hat{b}_{S,aS}^\dagger \hat{b}_{S,aS} \hat{b}_{S,aS} \rangle}{\langle \hat{b}_{S,aS} \rangle \langle \hat{b}_{S,aS} \rangle}.
$$

(5)

The power dependence for the intensity ratio $I_{as}/I_S$ and the $SaS$ field correlation $g^2(0)$ are described in panels (a) and (b) of Fig.1 respectively, for different values of the thermal phonon population $n_0$. While the Stokes field is found to be proportional to the excitation laser power $P_L$, the anti-Stokes field exhibits two different regimes. For lower power, thermal phonons dominate the process and $\langle n_{as} \rangle$ is proportional to $P_L$ (assuming there is no laser induced heating). For higher powers, the $SaS$ phenomenon dominates, and $\langle n_{as} \rangle$ is proportional to $P_L^2$ (see Supplementary Information for details). This rationale explains the results in Fig.1(a), $I_{as}/I_S$ being constant for low power, and for high power, $I_{as}/I_S \propto P_L$.

In Fig.1(b), the $SaS$ correlation function $g^2(0)$ is shown to be proportional to the inverse laser power, and it goes to a $n_0$-dependent constant value for small values of $P_L$.

The behaviors for $I_S$, $I_{as}$ and $g^2(0)$ observed by Kasperczyk et al. are, therefore, perfectly described by $\langle n_S \rangle_{ss}$, $\langle n_{as} \rangle_{ss}$ and $g^2(0)$ in Eqs.9 calculated by considering the model in Eqs.2-9. Here, $\langle n_{S,aS} \rangle_{ss}$ is the steady state number of $S,aS$ photons.

A rationale for $I_{as}/I_S$ that takes into account the $SaS$ phenomena can then be developed based on the theory for $\langle n_{as} \rangle_{ss}/\langle n_S \rangle_{ss}$. Setting $\lambda_S = \lambda_{as} = \lambda$, $\gamma_S = \gamma_{as} = \gamma$, $\lambda |\alpha|/\gamma_c \neq 0$, and considering the limit of $\gamma/\gamma_c \gg n_0$, the anti-Stokes/Stokes intensity ratio is given by

$$
\frac{\langle n_{as} \rangle_{ss}}{\langle n_S \rangle_{ss}} = \frac{n_0}{n_0 + 1} \exp \left[ \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2 P_L}{\gamma \gamma_c A} \right],
$$

(6)

which can be rewritten as

$$
\frac{I_{as}}{I_S} \approx C' \frac{n_0}{n_0 + 1} \left[ 1 + \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\lambda^2 P_L}{\gamma \gamma_c A} \right],
$$

(7)
where $C' = C_{aS}/C_S$, with $C_{S,aS}$ defined as the proportionality constant such that $I_{S,aS} = C_{S,aS}\langle n_{S,aS}\rangle_{ss}$. The constant $C'$ depends on the optical parameters, for instance, absorption coefficients, inelastic scattering cross sections and the dimension (geometry) of the sample under study [13].

Figure 2 shows a comparison of the experimental $I_{aS}/I_S$ results from the three-dimensional diamond (black data) [11], from a two-dimensional bi-layer graphene, where the layers are superposed in the so-called AB-staking configuration (AB-BLG, open red data) [10], and finally from the two-dimensional twisted bi-layer graphene (tBLG, solid red data), which was engineered to exhibit electronic resonance with the $aS$ photon emission [10].

The three different results observed for the three different samples in Fig. 2 can all be fit with Eq. 18, giving the parameters provided in Table I (see Supplementary Information for fitting details). Diamond can be fit with a dominant $SaS$ process ($(\lambda^2/\gamma\gamma c)A^{-1} = 23$) and a nearly constant temperature ($T \sim 295$ K). The AB-stacked bilayer graphene (AB-BLG) can be fit considering the $I_{aS}/I_S$ power dependence ruled by a linear dependence of the effective phonon temperature on laser power ($T = 295 + 30P_L$), with an irrelevant contribution from the $SaS$ phenomenon ($(\lambda^2/\gamma\gamma c)A^{-1} \equiv 0$). Finally, the twisted-bilayer graphene (tBLG) can be fit with a dominant $SaS$ process ($(\lambda^2/\gamma\gamma c)A^{-1} = 2700$) and a small contribution from laser induced heating ($T = 295 + 1.0P_L$). Due to resonance with the $aS$ photon emission, the assumption $\lambda_S = \lambda_{aS}$ should be discussed. Considering $\lambda_{aS} \neq \lambda_S$ does not change the overall picture, and more details can be found in the Supplemental Information.

Comparing the graphene samples, while in AB-BLG the generated phonons are mostly converted into heat, in tBLG they are mostly converted into light ($aS$ photons). But the most striking result is the much larger efficiency of the $SaS$ process in tBLG, with a $(\lambda^2/\gamma\gamma c)A^{-1}$ value that is two orders of magnitude larger than in bulk diamond. Besides these two orders of magnitude difference, the $P_L^2$ dependence for $I_{aS}$ in diamond can only be observed with the use of femtosecond lasers, where the pulse intensity is about $10^5$ times larger than the intensity of continuous wave laser radiation of the same average power. Furthermore, in bulk diamond the number of active atoms in the focal volume is $\sim 10^7$ times larger than in the two-dimensional graphene system. Finally, the ratio $I_{aS}/I_S$ at the highest power in tBLG reaches values of $\sim 0.5$, while in diamond $I_{aS}/I_S \sim 0.1$ was reached. Putting all numbers together, correlated $SaS$ generation per involved atom in the graphene-based system is roughly $10^{14}$ times more efficient than in bulk diamond.
Qualitatively, the reason for the striking efficiency of correlated SaS Raman scattering in the twisted bilayer graphene system might be related to a reduction in phase-space in the scattering event. In real space, the confined two-dimensional structure, which enhances electron-hole interactions in low-dimensional structures \[14, 15\], leads to a large overlap between the photon and phonon wavefunctions. In reciprocal space, the logarithmically diverging two-dimensional van-Hove singularity at the hexagonal saddle (M) point \[16\] strongly enhances the generation and recombination of electron-hole pairs at the aS photon energy \[10, 17\]. The SaS event is also expected to play a role in other low dimensional materials \[18\], where phase-space reduction becomes important. However, more theoretical work is needed to address the physics of the \(\lambda, \gamma, \) and \(\gamma_c\) parameters.

Raman spectroscopy is established as an important tool to study and characterize nanostructures \[2\]. It is surprising that the correlation between the Stokes and the anti-Stokes components can seriously affect \(I_{aS}/I_S\), being measurable indirectly from the intensity ratio. This aspect made it possible to measure the importance of the SaS correlation in graphene, where a direct \(g^2(0)\) measurement is not possible due to ultrafast luminescence \[19, 20\].

The stationary phonon population can then be analytically obtained from the steady state solution of Eq.3 and, in the limit of \(\gamma/\gamma_c \gg n_0\), it is given by

\[
\langle n_c \rangle_{ss} \approx n_0 \left( 1 + (n_0^{-1} + 2) \frac{\lambda^2 P_L}{\gamma \gamma_c A} \right).
\]  

The SaS event is an important decay channel that has to be explicitly considered when using Raman spectroscopy to extract structural and transport properties related to phonon anharmonicities in low-dimensional structures \[21\, 23\].

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AUTHOR CONTRIBUTIONS

CAPM performed the calculations. MFS idealized the theoretical framework. CHM helped to elucidate the connection between the theoretical framework and the available experimental results. AJ idealized the project and wrote the paper. All the authors discussed intensively the results and contributed on the final form of the manuscript.

COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.

Table I: Parameters used to fit the data from the three materials depicted in Fig.2 using Eq.18

Temperature *T* is given in K and laser power (*P*<sub>L</sub>) in mW. The other quantities are adimensional.

| MATERIAL | C<sup>′</sup> (λ<sup>2</sup> / γ<sub>c</sub>) A<sup>-1</sup> | *T*(*P*<sub>L</sub>) |
|----------|---------------------------------|------------------|
| diamond  | (34 ± 1) (23 ± 5) 295 + (0.02 ± 0.02)*P*<sub>L</sub> |
| tBLG     | (23 ± 1) (2700 ± 300) 295 + (1.0 ± 0.3)*P*<sub>L</sub> |
| AB-BLG   | (3.5 ± 0.2) 0 295 + (30 ± 2)*P*<sub>L</sub> |
Figure 1: Theoretical description of the Stokes and anti-Stokes intensity and correlation phenomena. (a) gives the population ratio $\langle n_{aS}\rangle_{ss}/\langle n_{S}\rangle_{ss}$, where $ss$ stands for steady state, and (b) gives the $SaS$ field correlation $g^2(0)$, according with Eqs. [9]. The excitation laser power $P_L$ dependences are plotted for different values of the thermal phonon population $n_0$ (see legend in (b)). We set $\lambda_S = \lambda_{aS} = \lambda$, $\gamma_S = \gamma_{aS} = \gamma$ and $P_0 \approx A\gamma_c / 2\lambda^2$ for $\gamma/\gamma_c \gg n_0$. The stationary phonon population gives nonphysical description for $P_L \geq P_0$ (more details in the Supplemental Information).
SUPPLEMENTAL INFORMATION: POWER DEPENDENCE OF KLYSHKO’S STOKES-ANTI-STOKES CORRELATION IN THE INELASTIC SCATTERING OF LIGHT

More details about the model

To analyze the Stokes and anti-Stokes populations and their respective correlation functions at zero time delay ($\tau = 0$), we computed the average values

$$
\langle n_{S,as} \rangle = \langle \hat{b}_{S,as}^\dagger \hat{b}_{S,as} \rangle, \quad \langle n_c \rangle = \langle \hat{c}^\dagger \hat{c} \rangle, \quad g^2(0) = \frac{\langle \hat{b}_{S}^\dagger \hat{b}_{aS} \hat{b}_{as} \hat{b}_{S} \rangle}{\langle \hat{b}_{S}^\dagger \hat{b}_{S} \rangle \langle \hat{b}_{aS}^\dagger \hat{b}_{aS} \rangle},
$$

which can be obtained by means of the equation

$$
\frac{\partial}{\partial t} \langle \hat{O} \rangle = i[\hat{H}, \hat{O}] + \text{Tr}(\hat{O} \mathcal{L} \hat{\rho}),
$$

Figure 2: Fitting the $I_{as}/I_S$ intensity ratio in three different solid state systems: three-dimensional diamond (black data), two-dimensional bi-layer graphene (AB-BLG, open red data), and two-dimensional twisted bi-layer graphene (tBLG, solid red data). Data points are experimental results from Refs. [11] (diamond) and [10] (graphene-systems), and lines are fit to the data using Eq. [18] and the parameters listed in table [1].
yielding the following linear system of differential equations:

\[
\begin{align*}
\partial_t \langle n_S \rangle &= -2\lambda_\alpha \text{Im}\{\langle \hat{c}_S \rangle \} - 2\gamma_S \langle n_S \rangle \\
\partial_t \langle n_{aS} \rangle &= -2\lambda_\alpha \text{Im}\{\langle \hat{c}^\dagger \hat{b}_S \rangle \} - 2\gamma_{aS} \langle n_{aS} \rangle \\
\partial_t \langle n_c \rangle &= -2\langle \gamma_c \rangle (\langle n_c \rangle - n_0) \\
\partial_t \langle \hat{c}_b \rangle &= -i\lambda_\alpha (\langle n_S \rangle + \langle n_c \rangle + \langle \hat{b}_S \hat{b}_{aS} \rangle) \\
&\quad - (\gamma_c + \gamma_S + i\omega_0) \langle \hat{c}_b \rangle - i\lambda_\alpha \\
\partial_t \langle \hat{c}^\dagger \hat{b}_{aS} \rangle &= -i\lambda_\alpha (\langle \hat{b}_S \hat{b}_{aS} \rangle - \langle n_c \rangle + \langle n_{aS} \rangle) \\
&\quad - (\gamma_c + \gamma_{aS} + i\omega_0) \langle \hat{c}^\dagger \hat{b}_{aS} \rangle \\
\partial_t \langle \hat{b}_S \hat{b}_{aS} \rangle &= -i\lambda_\alpha (\langle \hat{c}^\dagger \hat{b}_{aS} \rangle + \langle \hat{c}_b \rangle) \\
&\quad - (\gamma_S + \gamma_{aS} + i2\omega_0) \langle \hat{b}_S \hat{b}_{aS} \rangle.
\end{align*}
\]  

(11)

where \( \lambda_\alpha = \lambda|\alpha| \). Initially we will be setting \( \lambda_S = \lambda_{aS} = \lambda \) and \( \gamma_S = \gamma_{aS} = \gamma \). The dynamics will depend on how the incident field is implemented. In case of a pulsed laser, it is enough to redefine the coupling strength as a time-dependent function \( |\lambda_\alpha(t)|^2 = \lambda^2|\alpha|^2 f(t) \). \( f(t) \) can, for instance, be modelled as a temporal gaussian profile, such as \( f(t) = \exp(-t^2/2\sigma^2) \), where the coherence time is proportional to \( \sigma \). In that case there is not an steady state and, in order to analyze the behavior of the field population as a function of the laser power \( P_L \), we might consider measures at the excitation time, that is, the time at which the population gets its first maximum, or the time-averaged values of the observables defined in Eq. (9) as

\[
\langle \hat{O} \rangle_t = \lim_{\Delta t \to \infty} \int_0^{\Delta t} \langle \hat{O} \rangle_t dt / \Delta t.
\]

We first focus in the case of a continuum pumping, i.e., \( \lambda_\alpha(t) = \lambda_\alpha \) on the material. In this case, the system of differential equations (11) has steady state solution due to the environment-induced relaxation, which allows us for analytical solutions. We then write the system in (11) as a vectorial differential equation \( \partial_t \vec{x} = M \vec{x} + \vec{b} \), where \( M \) is a time-independent square matrix and

\[
\begin{align*}
\vec{x}^T &= (\langle \hat{n}_S \rangle, \langle \hat{n}_{aS} \rangle, \langle \hat{n}_c \rangle, \langle \hat{c}_b \rangle, \langle \hat{c}^\dagger \hat{b}_S \rangle, \langle \hat{c}^\dagger \hat{b}_{aS} \rangle, \langle \hat{b}_S \hat{b}_{aS} \rangle, \langle \hat{b}_{aS} \rangle, \langle \hat{b}_{aS} \rangle, \langle \hat{b}_{aS} \rangle) \\
\vec{b}^T &= (0, 0, 2\gamma_c n_0, -i\lambda_\alpha, i\lambda_\alpha, 0, 0, 0, 0, 0).
\end{align*}
\]

(12) \hspace{1cm} (13)

and set \( d_t \vec{x}_{ss} = 0 \), where \( ss \) stands for steady state. To solve this, we invert the matrix \( M \), which is only possible if \( M \) is not singular, i.e. if its determinant \( \text{Det}(M) \) is different
from zero. Then the solutions are given by \( \mathbf{x}^{\text{ss}} = -M^{-1}\mathbf{b} \). By simple inspection, it is straightforwardly noticed that the Stokes, anti-Stokes and phonon populations satisfy an equilibrium condition

\[ \langle \hat{n}_c \rangle^{\text{ss}} - n_0 = \frac{\gamma_c}{\gamma_c} (\langle \hat{n}_S \rangle^{\text{ss}} - \langle \hat{n}_{aS} \rangle^{\text{ss}}). \]  \( (14) \)

From this equation we might highlight two things. First, if the stationary solution for the phonons population approaches the thermal average number, \( \langle \hat{n}_c \rangle^{\text{ss}} \approx n_0 \), there is no absorption of incident photons, therefore Stokes modes generation, and since from Eq. (14) \( \langle \hat{n}_S \rangle^{\text{ss}} \approx \langle \hat{n}_{aS} \rangle^{\text{ss}} \), there will be no anti-Stokes modes. In this limit, if there is excitation of \( S \) - and \( aS \) -modes, they will be caused by thermal effects. This will be the case of high temperature \( (n_0 \gg 1) \), in which the heating of the sample favours random photon radiation. Secondly, in the low temperature limit \( (n_0 \ll 1) \) we see that the excitation of even a single photon produces \( S \)-\( aS \) fields with low intensity, where the anti-Stokes field will be less intense.

One of the central results in the paper is to show the behavior of the Stokes-anti-Stokes field intensities in terms of the power laser. We can obtain an analytical expression for those intensities, \( I_{S,aS} \), which are proportional to the average population of the photon modes \( \langle \hat{n}_{S,aS} \rangle^{\text{ss}} \). For \( S \) - and \( aS \) -modes we find

\[ \langle n_S \rangle^{\text{ss}} = \frac{2(1 + n_0)\tilde{\gamma}(1 + \tilde{\gamma})\tilde{\lambda}_\alpha^2 - (3 + 4n_0 + 2\tilde{\gamma})\tilde{\lambda}_\alpha^4}{2(\tilde{\gamma} + \tilde{\gamma}^2 - 2\tilde{\lambda}_\alpha^2)(\tilde{\gamma}(1 + \tilde{\gamma}) - (1 + 2\tilde{\gamma})\tilde{\lambda}_\alpha^2)}, \]  \( (15) \)

\[ \langle n_{aS} \rangle^{\text{ss}} = \frac{2n_0\tilde{\gamma}(1 + \tilde{\gamma})\tilde{\lambda}_\alpha^2 - (1 + 4n_0 - 2\tilde{\gamma})\tilde{\lambda}_\alpha^4}{2(\tilde{\gamma} + \tilde{\gamma}^2 - 2\tilde{\lambda}_\alpha^2)(\tilde{\gamma}(1 + \tilde{\gamma}) - (1 + 2\tilde{\gamma})\tilde{\lambda}_\alpha^2)}, \]  \( (16) \)

where \( \tilde{\gamma} = \gamma/\gamma_c \) and \( \tilde{\lambda}_\alpha = \lambda_\alpha/\gamma_c \). Note that \( \tilde{\lambda}_\alpha^2 = (\tilde{\lambda}_\alpha^2 / A) P_L \). The above solutions are well behaved, i.e., \( \text{Det}(M) \neq 0 \), and are physically meaningful if \( \langle \hat{n}_{S,aS} \rangle^{\text{ss}} \geq 0 \); these conditions are fulfilled if \( \tilde{\lambda}_\alpha < \sqrt{\tilde{\gamma}(\tilde{\gamma} + 1)/(1 + 2\tilde{\gamma})} \). Therefore our description is valid if below the laser power upper bound

\[ P_0 \equiv A \frac{\tilde{\gamma}(\tilde{\gamma} + 1)}{\tilde{\lambda}_\alpha^2(1 + 2\tilde{\gamma})}, \]  \( (17) \)

Note that for low laser power both \( \langle n_{S,aS} \rangle^{\text{ss}} \) increase linearly with \( P_L \). In order to easily identify different regimes for \( P_L \), the intensities ratio \( I_{aS}/I_S \) is a good figure of merit. If
\[ \gamma \gg \{n_0, 1\} \text{ and } \tilde{\lambda}_a \neq 0, \text{ then } I_{aS}/I_S \text{ reduces to} \]

\[
\frac{\langle n_{aS} \rangle_{ss}}{\langle n_S \rangle_{ss}} = \frac{n_0}{n_0 + 1} \left[ \frac{1 + (\tilde{\lambda}^2/A\tilde{\gamma}n_0)P_L}{1 - (\lambda^2/A\tilde{\gamma}(n_0 + 1))P_L} \right]
\]

\[
\frac{I_{aS}}{I_S} \approx C' \frac{n_0}{n_0 + 1} \exp \left\{ \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\tilde{\lambda}^2}{A\tilde{\gamma}}P_L \right\}
\]

\[
\approx C' \frac{n_0}{n_0 + 1} \left[ 1 + \left( \frac{1}{n_0} + \frac{1}{n_0 + 1} \right) \frac{\tilde{\lambda}^2}{A\tilde{\gamma}}P_L + O(P_L^2) \right],
\]

(18)

which differs from Eqs.(6,7) in the paper due to the introduction of \( \tilde{\gamma} \) and \( \tilde{\lambda}_a \), used here to simplify the notation. We chose not to use this notation in the paper to keep the equations related to the fundamental constants. Here \( C' = C_{aS}/C_S \), with \( C_{aS}, C_S \) defined as the proportionality constant such that \( I_{S,aS} = C_{S,aS}\langle \hat{n}_{S,aS} \rangle_{ss} \). The phonon population can also be analytically obtained from the stationary analysis and it is given by

\[
\langle \hat{n}_c \rangle_{ss} = \frac{n_0 \tilde{\gamma}(1 + \tilde{\gamma}) + (\tilde{\gamma} - n_0)\tilde{\lambda}^2/A P_L}{\tilde{\gamma}(1 + \tilde{\gamma}) - (1 + 2\tilde{\gamma})\tilde{\lambda}^2/A P_L}
\]

which is only valid if \( \tilde{\lambda}_a < \sqrt{\tilde{\gamma}(\tilde{\gamma} + 1)/(1 + 2\tilde{\gamma})} \). In the case \( \tilde{\gamma} \gg 1 \), the phonon population reduces to

\[
\langle \hat{n}_c \rangle_{ss} \approx n_0 \left( 1 + (n_0^{-1} + 2) \frac{\tilde{\lambda}^2}{A\tilde{\gamma}}P_L \right) + O(P_L^2).
\]

(19)

Note that if \( P_L \neq 0 \), which activates the \( S-aS \) modes, the photon population is always larger than \( n_0 \), therefore the difference \( \langle \hat{n}_S \rangle_{ss} - \langle \hat{n}_{aS} \rangle_{ss} > 0 \).

There are additional effects that allow us for a sofistification of our effective description. We might also consider effects of phase noise caused by scattering of generated phonon with different momenta. This is done by adding an extra Lindbladian term

\[
\mathcal{L}'(\hat{\rho}) = -\gamma'_c (\hat{\rho} \hat{\rho}^* + \hat{\rho}^* \hat{\rho} - 2\hat{n}_c \hat{\rho} \hat{n}_c).
\]

(20)

It is easily proven, using Eq. (10), that phase noise does not modify the equations for the populations in Eqs. (15) and (16) therefore, the equilibrium condition is preserved. Its main changes are for equations of the expected values of the type \( \langle \hat{c} \hat{b}_S \rangle \) and \( \langle \hat{c}^\dagger \hat{b}_{aS} \rangle \), introducing expectation values of second-order operators, as for instance \( \langle \hat{c} \hat{b}_S \hat{n}_c \rangle \). The new system of equations is not trivial and analytical solutions are no longer easy to obtain. In that case, and for the
computation of correlation functions \( \langle \hat{b}_x^\dagger \hat{b}_{x'}^\dagger \hat{b}_{x''} \hat{b}_{x'''} \rangle \) \((x = S, aS)\), we compute the stationary solution for the density operator \(\hat{\rho}_{ss}\), for which \(d_t \hat{\rho}_{ss} = 0\). We must thus solve \(\mathcal{L}_{\text{total}} \hat{\rho}_{ss} = 0\), which requires an expansion in the Fock basis \(\{|n_S, n_{aS}, n_c\} \in \mathcal{H} = \mathcal{H}^S \otimes \mathcal{H}^{aS} \otimes \mathcal{H}^c\). Yet, this basis increases exponentially and must be truncated for practical implementations. After numerically obtaining \(\hat{\rho}_{ss}\) we can compute expected values as \(\langle \hat{O} \rangle_{ss} = \text{Tr}(\hat{O} \hat{\rho}_{ss})\), and shall be able to analyze changes on the population of the photonic modes and S-aS correlation functions in terms of the system parameters.

It remains to be discussed the effect of \(\lambda_S \neq \lambda_{aS}\), which is important when resonance effects are in place. Considering \(\lambda_S > \lambda_{aS}\), with \(\frac{\lambda_{aS}}{\lambda_S} = \varepsilon\) and \(\varepsilon < 1\), we can set \(\lambda_S = \lambda\) and \(\lambda_{aS} = \varepsilon \lambda\). Then Eq.(7) in the paper would be changed to:

\[
\frac{\langle n_{aS} \rangle_{ss}}{\langle n_S \rangle_{ss}} \approx \varepsilon^2 \frac{n_0}{n_0 + 1} \exp \left[ \frac{\lambda^2 |\alpha|^2}{\gamma_c \gamma} \left( \frac{\varepsilon^2}{n_0 + 1} + \frac{1}{n_0} \right) \right].
\]

(21)

Otherwise, if \(\lambda_S < \lambda_{aS}\), with \(\frac{\lambda_{aS}}{\lambda_S} = \varepsilon\) and \(\varepsilon < 1\), we can set \(\lambda_{aS} = \lambda\) and \(\lambda_S = \varepsilon \lambda\). Then Eq.(7) in the paper would be changed to:

\[
\frac{\langle n_{aS} \rangle_{ss}}{\langle n_S \rangle_{ss}} \approx \frac{1}{\varepsilon^2} \frac{n_0}{n_0 + 1} \exp \left[ \frac{\lambda^2 |\alpha|^2}{\gamma_c \gamma} \left( \frac{1}{n_0 + 1} + \frac{\varepsilon^2}{n_0} \right) \right].
\]

(22)

We will discuss the importance of \(\lambda_S \neq \lambda_{aS}\) in the results of tBLG in section.

MORE THEORETICAL RESULTS

Figure 3 presents how populations depend on the laser power \(P_L\) for \(\tilde{\gamma} = 100\) and different thermal phonon numbers \(n_0\). For \(n_0 \neq 0\) and low laser power, both photonic modes increase linearly with \(P_L\), with a slope proportional to \((n_0 + 1)\) for S-modes and \(n_0\) for aS-modes. In the limit of extremely low temperature \((n_0 \rightarrow 0)\) the aS-modes always increase with \(P_L^2\), but for a non-zero temperature there are two regimes for the growth of the aS population, i.e., \(I_{aS} \propto P_L\) for low laser power and \(I_{aS} \propto P_L^2\) for high laser power. Note that for \(P_L \neq 0\) there exists activation of S- and aS-modes due to the inelastic scattering, however random generation of photonic modes is also expected due to the presence of the thermal bath of phonons. The interplay between these two processes will affect the production of photon pair S-aS, i.e. the SaS event.

The two regimes are also reflected in the results for cross-correlation function \(g^2(0)\), as shown in Fig. 4. Note that the presence of phase noise \((\gamma'_c \neq 0)\) does not affect relevantly
Figure 3: Panel (a) presents Stokes ($S$), anti-Stokes ($aS$) and phonon ($Ph$) populations as a function of the laser power $P_L$ in units of $P_0$. The different curves correspond to different temperatures set by the thermal average number $n_0$ (see legend in panel (b)). In panel (b) we show the ratio between $aS$ and $S$ mode population as a function of $P_L$ and $n_0$. For this figure we set $\tilde{\gamma} = 100$, $\gamma_c' = 0$ and a continuum pumping.

the phenomenology presented in this work (see Fig. 4). Nevertheless, for very large values of $P_L$ the convergence of our numerical fails due to the truncation of the Hilbert space, and the results are not conclusive due to the lack of sufficient resources to tackling that regime.

So far our analysis has been done for continuum pumping, which allows for well behaved steady state solutions. When considering a time-dependent but short-time pumping, the system response is similar in shape to the implemented pulse and an steady state is not expected. In that case, as mentioned before, we computed the long-time averages of the observables of interest. The results for the photonic populations are shown in Fig. 5 in comparison with the steady state solution for continuum pumping. It is clearly seen that the phenomenology studied throughout this paper is preserved, that is, the different regimes of the populations with the increasing laser power $P_L$ is preserved, and only changes in the intensity of the $S$- and $aS$-modes are observed. The results in Fig. 5 allows us to generalize
Figure 4: (a) Stokes (upper lines) and anti-Stokes (lower lines) modes populations as a function of the normalized laser power ($P_L/P_0$) for different values of $\gamma'_c/\gamma_c$ (different line colors, see legend). (b) The effect of $\gamma'_c/\gamma_c$ on $g^2(0)$ for different values of $n_0$ (see legends). Other parameters are same as those in figure 3.

We finally want to remark that our theory is based on phenomenological constants that will depend on the material under study. The validity of the approximations made to obtain analytical expressions for the ratio $I_{aS}/I_S$ and the phonon population $\langle n_c \rangle$ is supported by typical and relevant parameters as $n_0$, $\gamma$ and $\gamma_c$. In typical experiments, like the one reported in Ref. [1], $n_0 = 1.6 \times 10^{-3}$ at $T = 295$ K, $1/\gamma_c \approx 10^{-12}$ s (phonon lifetime) and $1/\gamma \approx 130 \times 10^{-15}$ s (laser pulse width). The $\gamma/\gamma_c$ is at least one order of magnitude larger than one, and four orders of magnitude larger than $n_0$. The incident field has a power range from 1 mW to 1 W and wavelength 785 nm. The number of incident photons is of the order of $|\alpha|^2 \sim 52 \times 10^6 - 52 \times 10^9$ per pulse.

About the Analysis of the Experimental Data

A fair question one can ask is whether the experimental results for $I_{aS}/I_S$ from diamond [1] and graphene [2] cannot be satisfactorily fit considering just the Bose-Einstein distribution function. In other words, does the data on the power dependence of $I_{aS}/I_S$ from diamond
Figure 5: Stokes (lines) and anti-Stokes (lines with squares) modes populations as a function of the normalized laser power ($P_L/P_0$) for different types of incident laser (see legend). The inset shows the time profile of the implemented lasers. The parameters are same as those in figure 3 with $n_0 = 10^{-3}$.

and graphene provide convincing case that anything beyond laser heating has been observed?

The presence of the $SaS$ correlation in diamond is unquestionable due to the results of the correlation function $g^2(0)$ [1]. As discussed in our paper, our theory provides perfect description for the excitation power dependence of $I_{aS}$, $I_S$, $I_{aS}/I_S$ and $g^2(0)$. The AB-BLG is fit in our work considering that the $I_{aS}/I_S$ is ruled by thermal effects and, although relatively good fitting can be obtained with a small contribution from the $SaS$ phenomenon, we raise no controversy in this case. We now discuss results for the tBLG sample [2], which according to our analysis, is fully dominated by the $SaS$ phenomenon.

Figure 6 is a plot of what would be the sample temperature $T$, if extracted directly from the $I_{aS}/I_S$ experimental data and using the Bose-Einstein phonon distribution function, which from Eq.(1) in the paper is given by:

$$T = \frac{E_{ph}}{k_B \left[ \ln C - \ln \frac{I_{aS}}{I_S} \right]}, \quad (23)$$

where $E_{ph}$ is the phonon energy, $k_B$ is the Boltzmann constant, and $C$ is the proportionality constant that accounts for all the optical properties of the setup and sample. $C$ is chosen
such that $T \rightarrow 295 \, \text{K}$ as $P_L \rightarrow 0$. For tBLG we obtain $C^{tBLG} = 26$ and for the AB-BLG we obtain $C^{tBLG} = 4$. The fact that $C^{tBLG} > C^{tBLG}$ is expected, since tBLG was engineered for specific resonance behavior. However, the fact that $T$ is generally larger for tBLG, as compared to AB-BLG (see data in Fig.6) is not expected. First, the tBLG was engineered for resonance with the anti-Stokes photon emission. Therefore it is expected that this sample would have a stronger cooling channel, and it would actually exhibit lower temperatures than the AB-BLG. Second, this expectation is proven to be correct by the lower shift in phonon frequency observed for tBLG, as shown in Ref. [2]. Therefore, the tBLG can not be hotter than the AB-BLG, and the result obtained with Eq.23 is proven to be inconsistent.

Figure 6: Expected effective temperature $T$ for tBLG (red) and AB-BLG (blue), extracted directly from the $I_{aS}/I_S$ data [2], according to Eq.23, i.e. neglecting the $SaS$ phenomena.

Finally, one can also argue on how sensitive the data fitting is with respect to the parameters choice. Parameter values outside the errors given in table I of the paper do not fit the data properly. Figure 7 shows three possible fittings of the tBLG data. The red line is the best fit, as given in the main paper. The black and blue lines were obtained by considering that the $I_{aS}/I_S$ is ruled by pure $SaS$ phenomena and by pure thermal phenomena, respectively. Notice that these two fitting options do not fit the data properly. The worse fitting is obtained using the pure thermal phenomena, demonstrating the predominance of the $SaS$
phenomena, like in diamond.

Figure 7: Three different fittings for the $I_{aS}/I_S$ data from tBLG [2]. The red points are the $I_{aS}/I_S$ data. The red line is the same fitting as in the paper. The black line is a fit to the data using Eq.(7) from the paper, with $C' = 23$, $(\lambda^2/\gamma\gamma c)A^{-1} = 4000$ and $T = 295$. The blue line is a fit to the data using Eq.(7) from the paper, with $C' = 23$, $(\lambda^2/\gamma\gamma c)A^{-1} = 0$ and $T = 295 + 30P_L$.

Finally, we now discuss the possibility of $\lambda_s \neq \lambda_{aS}$. In non-resonant scattering, $\lambda_s = \lambda_{aS}$ is expected due to time-reversal symmetry. This is the case for diamond [1]. If resonance with electronic states exists, but there is not much difference between the resonance with the $S$ and $aS$ photon emission, then $\lambda_s \sim \lambda_{aS}$. This is the case of AB-BLG, where the density of states does not vary too much between the $S$ and $aS$ photon energies [2]. However, in the case of tBLG, the electronic structure is engineered to exhibit specific resonance with the $aS$ photon emission [2], i.e. $\lambda_{aS} > \lambda_s$. Therefore, strictly speaking, Eq.22 from this Supplemental Information should be used to fit the data, rather than Eq.(7) from the paper. The value of $\varepsilon$ is easily obtained from the data if we consider that this parameter rules the enhancement of $C'$ from tBLG as compared to AB-BLG. From table I in the paper and Eq.22 from this Supplemental Information we obtain $\varepsilon^2 = 3.5/23$. If we now add $\varepsilon = 0.39$
in Eq. 22 from this Supplemental Information and fit the data, we obtain a fitting curve
that superimpose to the fitting curve used in the paper by setting \((\lambda^2/\gamma_c)A^{-1} = 3900\). Therefore, considering the possibility of \(\lambda_S \neq \lambda_aS\) in our analysis actually enhances the
importance of the \(SaS\) phenomena in tBLG. We chose to keep the simpler equation in the
paper since the general picture does not change, and the discussion is simpler.

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