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Lucas V. Carvalho, Tiago A. Freitas, Paula Machado Sr., Raul Correa, Marcelo F. Santos, Carlos H. Monken, Ado Jorio, "Properties of correlated Stokes-anti-Stokes Raman scattering from diamond," Proc. SPIE 12228, Ultrafast Nonlinear Imaging and Spectroscopy X, 1222803 (3 October 2022); doi: 10.1117/12.2633272

SPIE.

Event: SPIE Optical Engineering + Applications, 2022, San Diego, California, United States

Properties of correlated Stokes-anti-Stokes Raman Scattering from Diamond

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ABSTRACT

The correlated Stokes-anti-Stokes Raman scattering mediated by phonons was introduced in 1977 by Klyshko. In the last two decades, it has been broadly studied experimentally, including results on diamond, graphene and transparent liquid. The theoretical description of non-resonant Stokes-anti-Stokes pair production was shown to be formally similar to the BCS theory of superconductivity, raising attention to the study of pair production as a function of the Raman shift. Intriguingly, the pair production efficiency is not symmetric with respect to the positive versus negative detuning from phonon resonance, a result that was shown for a 180fs pulsed laser, and that remains without a theoretical explanation. Here we show the asymmetry is persistent in diamond measured with lasers of different pulse widths (180 fs and 5 ps) and different wavelengths (633 nm versus 785 nm).

Keywords: Raman scattering, correlated photons, Stokes-anti-Stokes correlation, diamond, nonlinear optics

1. INTRODUCTION

Raman scattering is the inelastic scattering of light by matter. In the particle picture, a photon can be scattered by a phonon, which is the quantum analog to photons, the phonons quantizing the vibrational energies of the atoms in molecules or solids. When scattered by the phonon, the photon can gain or lose energy, these processes being called anti-Stokes or Stokes scatterings, respectively[1].

The number of phonons in a material is generally related to the material´s temperature, with the thermal population of phonons given by the Bose–Einstein distribution function. Since Stokes and anti-Stokes processes are related to the probability to create and annihilate a phonon in the photon-phonon scattering, respectively, the intensity ratio between the Stokes and anti-Stokes processes can be utilized to measure material´s local temperature, as determined by the quantum theory of the harmonic oscillator[1,2].

One aspect that is not considered in this type of thermal treatment, however, is the possibility that one single phonon that is created in the Stokes process is subsequently annihilated in the anti-Stokes process (see figure 1). This correlated Stokes-anti-Stokes scattering (SaS) phenomenon was proposed in 1977 by Klyshko[3], and it has been shown to affect the anti-Stokes and Stokes intensities in graphene[4,5], diamond[6-8] and transparent liquids[9,10]. A theoretical framework to address this phenomenon has been proposed, focusing on implications for the anti-Stokes/Stokes intensity ratio[1], and the photon wavefunction formalism has also been utilized to describe the SaS dynamics[11,12].

Therefore, besides a generalization of the Bose-Einstein population function for Raman spectroscopy[1], the theoretical description shows intriguing similarities with the Cooper pair formation in the BCS theory for superconductivity[10]. The properties of the generated “photonic Cooper pairs" have been studied, including the dependence of the SaS pair generation as a function of the Raman shift, scattering momenta and time delay and polarization, all for a 180 fs pulsed laser at 633 nm wavelength[7,8]. In this work we will present the spectral distribution of the correlated Stokes and anti-Stokes Raman scattering from diamond, addressing how the SaS production efficiency depends on the Raman shift, for two pulsed laser with different pulse time-width, namely a 180 fs and a 5 ps pulsed laser at 785 nm wavelength.

Ultrafast Nonlinear Imaging and Spectroscopy X, edited by Zhiwen Liu, Demetri Psaltis, Kebin Shi, Proc. of SPIE Vol. 12228, 1222803
 · 0277-786X · doi: 10.1117/12.2633272

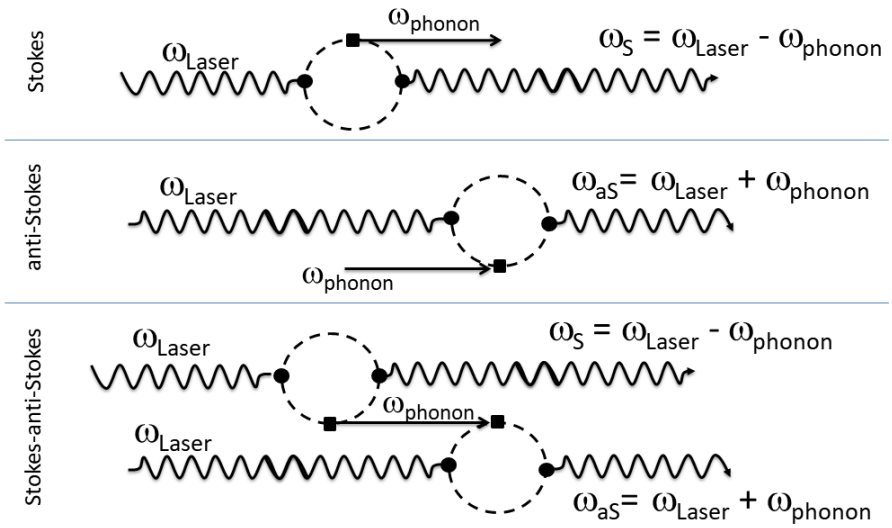

Figure 1. Feynman diagrams for the Stokes, anti-Stokes and correlated Stokes-anti-Stokes Raman scattering processes. Wavy lines indicate photons and straight lines indicate phonons.

2. METHODS

The experiment setup utilized for the experimental results shown here is displayed in figure 2.

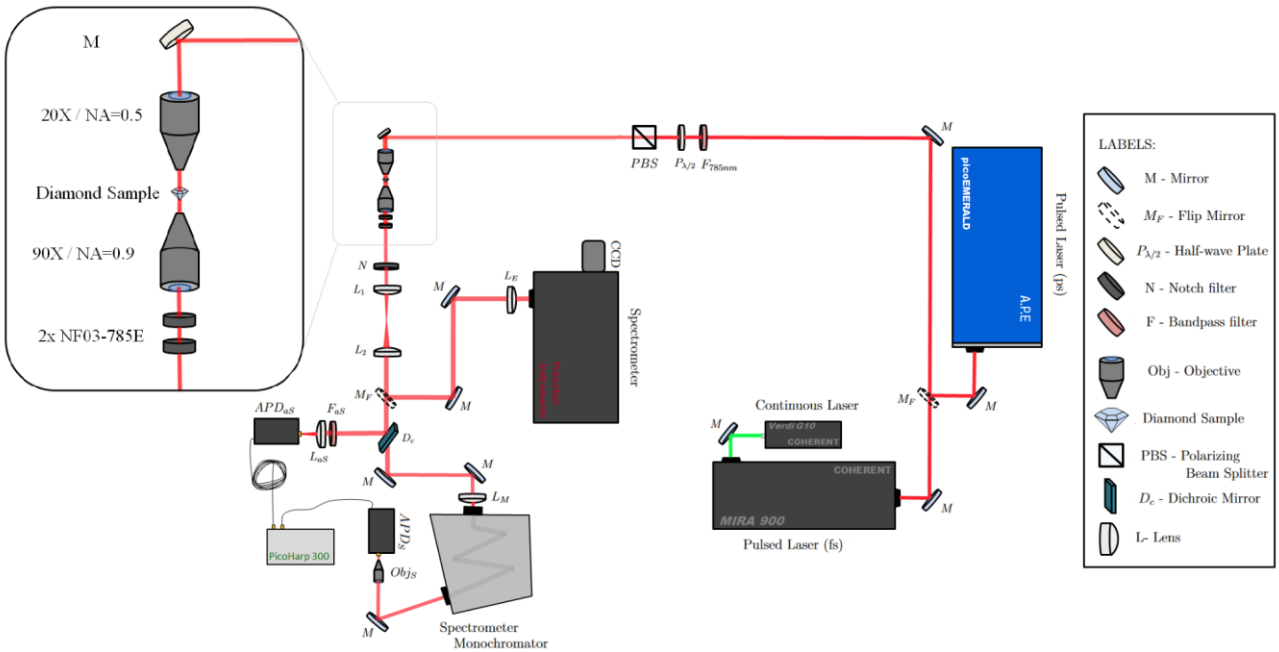

Figure 2. Schematics of the experimental setup. All the elements utilized are described in the figure. NA stands for numerical aperture of the objectives. The dichroic mirror is utilized to separate the Stokes (S) and anti-Stokes (aS) beams, driving the S and aS photons to the APD_S and APS_{aS}, respectively.

A diamond sample is excited with either a 5 ps or a 180 fs pulsed laser. The wavelengths were 785 nm for both lasers. Avalanche photodiodes (APDs) connected to a time-correlated single photon counting module are utilized to measure the SaS correlated photons. The spectrometer monochromator is utilized to filter the Stokes frequency range going to the Stokes APD. The spectrometer with a charged-coupled device (CCD) is utilized only for spectral check of the measured photons. More details on the experimental apparatus can be found in our previous publications[6-9].

3. RESULTS

Figure 3 shows the number of Stokes-anti-Stokes correlated photons measured as a function of Raman shift, for two pulsed lasers: (a) a 180fs laser and (b) a 5ps laser.

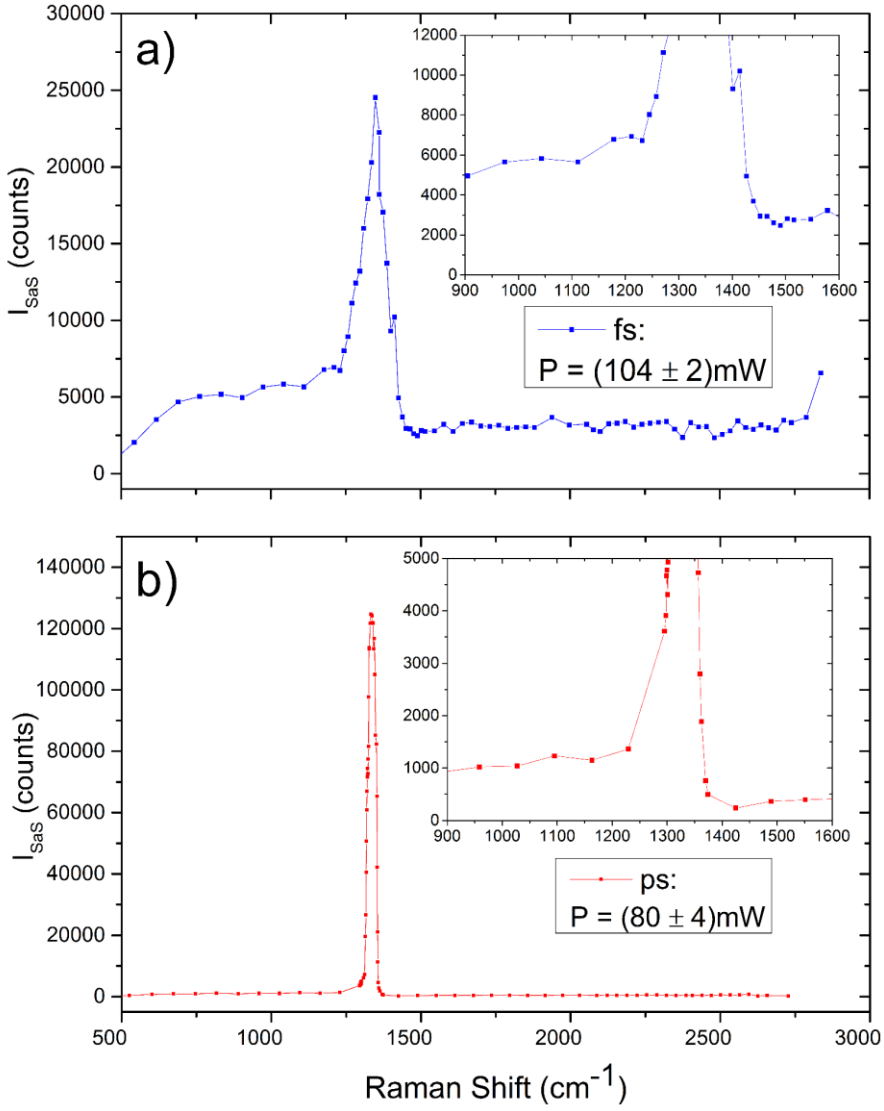

Figure 3. Number of Stokes-anti-Stokes correlated photons measured as a function of Raman shift, for two pulsed lasers: (a) a 180fs laser and (b) a 5ps laser, both at 785 nm wavelength.

In both cases excitation was given by 785 nm wavelength lasers. For each point, we accumulated the signal for 600 seconds, and the values shown here have been corrected to account for the system's efficiency. The insets are zooms to the baseline near the diamond phonon frequency 1332 cm^{-1}. The excitation laser powers reaching the sample in the two cases are also provided in the figure.

Both measurements show the same qualitative behavior: (i) a peak of SaS emission when looking at the diamond phonon energy, i.e. 1332 cm^{-1}. The spectral widths of the 1332 cm^{-1} SaS peaks are dictated by the widths of the excitation lasers; (ii) an asymmetric pair production when moving away from the phonon resonance to smaller versus greater Raman shifts, with more SaS emission at lower Raman shifts and less Raman emission when moving to larger Raman shifts. Consistent results were observed before for a 180fs laser at 633 nm wavelength[7], and these results are here evident for a 5ps pulse, which is sharper in linewidth, also evidencing a clear and more abrupt asymmetry. When comparing the SaS production between fs and ps lasers, more pairs are produced in the fs regime, consistent with the compression of a larger number of phonons in the shorter pulse, adequate for the non-linear SaS process.

4. CONCLUDING REMARKS

Stokes-anti-Stokes correlated emission in diamond as a function of Raman shift is studied here, utilizing two different pulsed lasers, a 180 fs and a 5 ps pulse width laser. The frequency spread (width) of the phonon resonance peak is dictated by the laser widths, being sharper in the ps laser. Pair production is more efficient in the fs case, in agreement with expectation for a non-linear effect. Furthermore, the Stokes-anti-Stokes Raman pair production efficiency is not symmetric with respect to the positive versus negative frequency detuning from the phonon resonance. This result was shown before for a 180 fs pulsed laser at 633 nm wavelength[7], and here we show the asymmetry is persistent in diamond measured with lasers of different pulse widths (180 fs and 4 ps) and different wavelengths (633 nm and 785 nm). This asymmetry remains without a theoretical explanation and we hope our results will foster interest in the problem.

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