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Stimulated Raman scattering: old physics, new applications

Vladislav V. Yakovlev¹, Georgi I. Petrov¹, Hao F. Zhang², Gary D. Noojin³, Michael L. Denton³, Robert J. Thomas⁴, and Marlan O. Scully^{5,6}

¹Department of Physics, University of Wisconsin - Milwaukee, Milwaukee, WI 53201, USA

²Department of Electrical Engineering, University of Wisconsin - Milwaukee, Milwaukee, WI 53201, USA

³Life Sciences Research and Applications Department, Northrop Grumman, San Antonio, TX 78228

⁴U.S. Air Force Research Laboratory, 711th HPW/RHDO, Brooks City-Base, TX 78235

⁵Department of Physics, Texas A&M University, College Station, TX 77840

⁶Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544

Abstract

Stimulated Raman scattering as a promising way of expanding the tunability of ultrafast lasers and as an exciting new biomedical imaging modality capable of selective excitation and chemically-specific diagnostics of molecular species.

Keywords

Raman; stimulated Raman; ultrashort laser pulses; biomedical imaging

1. Introduction

Stimulated Raman scattering was first discovered by an accident, when a cell with nitrobenzene was introduced inside a ruby laser cavity [1]. On the output, Woodbury and Ng observed a rather strong emission at the wavelength other than the fundamental wavelength of ruby laser, 694.3 nm. While initial explanation suggested the presence of some sort of fluorescence/ luminescence emission, later it was realized that it is a two-photon process, schematically presented in Fig. 1, which can be fully described by quantum mechanical calculations [2]. Later, Garmier et al [3] and Bloembergen and Shen [4–5] introduced the coupled-wave formalism to describe the stimulated Raman effect. The very first experimental observation of stimulated Raman scattering (SRS) has clearly demonstrated the great potential of this technique (i) to generate new colors of light and (ii) to dramatically enhance the efficiency of weak Raman transition. We have recently revisited those two applications, and, in the report, we describe our recent results (i) one developing high-repetition rate discretely tunable picoseconds laser system based on a very efficient Raman amplification and (ii) on introducing a novel optical imaging modality based on selective stimulated Raman excitation with the following acoustic imaging of the area, which was the most affected by such an excitation.

2. Theoretical background

A schematic diagram of SRS is shown in Fig. 1. The incident light at frequency ω_1 produces spontaneous Raman scattering at frequency ω_2 . In the simplest form, it can be considered as a loss of one quantum at frequency ω_1 and a gain of another at frequency ω_2 . If we consider the average number of quanta in a single mode of the wave ω_2 per unit length, $\bar{n}_2$, then (see, for example, [6])

$$\frac{d\bar{n}_2}{dz} = (G_R - \alpha_2) \bar{n}_2, \quad (1)$$

where α_2 is a linear absorption, and

$$G_R = N \frac{4\pi^2 c^3 \varepsilon_1}{\omega_1 \omega_2^2 \varepsilon_2} \frac{\rho_i - \rho_f}{\rho_i} \left(\frac{d\sigma}{d\Omega} \right) |E_1|^2 g(\hbar\Delta\omega). \quad (2)$$

Here, $\varepsilon_1, \varepsilon_2$ is the dielectric function at corresponding light frequencies, ρ_i, ρ_f are the populations of the two states, i and f , $d\sigma/d\Omega$ is the differential Raman cross-section, E_1 is the amplitude of the electric field on the incident frequency, and function $g(\hbar\Delta\omega)$ describes the density of states for the Raman transition, i.e. the shape of the Raman line (here, and later we consider only the on resonant transition, i.e. $g(0) = 1$). Eqs. (1–2) describe the major underlying physics of SRS. From Eq. (1), it is clear that if the Raman gain, G_R , exceeds the absorption loss in the medium, the number of photons at frequency ω_2 will experience an exponential growth with the distance of the wave's propagation, L .

To characterize this amplification process, it is intuitive to introduce a factor of merit, $F.O.M. = G_R L$. Assuming that there is no self-focusing, one can see that Raman gain is proportion to the incident light intensity, which, in its turn proportion to the incident power and inverse proportional to the square area of the cross-section, A . For a diffraction-limited beam, $A = \pi w_0^2$, and $L \cong \pi w_0^2 / \lambda_1$, where w_0 is the beam-waist, λ_1 is the wavelength of light. Evaluation of the figure of merit leads to conclusion that the efficiency of Raman amplification depends only on the incident power of the laser beam. This result has an important consequence for the light generation via SRS process: for a given input power, only a certain gain can be achieved. To achieve a substantial energy level in the amplified pulse one has to provide a strong enough seed pulse to overcome the gain limitation in low pump power SRS amplifier system.

The second important observation is related to the energy balance. Assuming that there is no phase-matching, and no significant anti-Stokes wave is generated, the residual energy ($\hbar\omega_1 - \hbar\omega_2$) will be converted into heat. Further assuming a thermal energy balance, one can calculate the temperature rise of the irradiated volume to be 10's of mK [7–8]. This temperature rise happens in a very short period of time resulting in thermoelastic expansion of the sample leading to the generation of photoacoustic waves [9]. The later can be detected by an externally placed ultrasonic transducer [9–10]. If two waves are incident upon the medium with a vibrational frequency Ω , the maximum signal detected by a transducer will be achieved when the difference frequency is exactly equal the frequency of vibrational transition. By varying the position of one frequency with respect to the other and by simultaneous measurement the amplitude of photoacoustic wave, one can obtain the Raman spectrum of the medium [11–12]. Alternatively, by setting the difference frequency to be equal to the vibrational frequency of a certain chemical, i.e. $\omega_1 - \omega_2 = \Omega$, and scanning the position of the sample by simultaneous

detecting the amplitude of the photoacoustic wave, the distribution of a specific chemical substance, characterized by the Raman transition, Ω , will be recorder [8].

3. High repetition rate Raman amplifier

Optical frequency conversion of ultrashort laser pulses is an indispensable way of extending the tunability of laser radiation. The most common approach to attain widely tunable ultrashort laser pulses is to use optical parametric oscillator [13] or parametric amplifier [14–15] for down-conversion and sum frequency generation for up-conversion. Many spectroscopic applications, such as microspectroscopy, cannot utilize a lot of energy due to the intensity constrains in the focal plane of the laser beam and would greatly benefit from the availability of broadly tunable laser sources at the repetition rate of the order of 1 MHz. In the same time, for applications like UV Raman spectroscopy it is important to maintain a narrow band pulse in order to preserve the adequate spectral resolution.

As it was pointed out earlier, the major difficulty of achieving light amplification by means of SRS is the lack of the sufficient input power of the pump pulse. We have recently solved this problem by providing a strong seed pulse to minimize the gain requirements.

The seed pulse is provided through broadband continuum generation in Ge-doped fiber (Nufern, Inc.). The schematic of the experimental set-up is shown in Fig. 2. In brief, picosecond pulses from a low-repetition rate Nd:YVO₄ oscillator [16] are further amplified in a four-pass diode-pumped Nd:YVO₄ amplifier. The output is split in such a way that about 1 μ J is sent into 1-meter-long fiber, and the rest of the energy is used to pump a 20-mm-long YVO₄ crystal. The later has been choose because of it is wide availability and a strong Raman cross-section. A typical Raman-loss spectrum is shown in Fig. 3 for different polarization orientations for two incident beams. The strongest line corresponds to the Raman transition at 880 cm^{-1} with the characteristic full-width-half-maximum linewidth, $\Gamma = 3\text{ }cm^{-1}$. The output spectrum from a fiber is shown in Fig. 4. Strong Raman cross-section of Ge-doped fibers promotes stimulated Raman scattering in those fibers, leading to a very power, red-shifted continuum generation in those fibers [16–17]. With as little as 1 μ J of the pump energy, we were able to achieve almost 50% efficient energy conversion of the pump into the first Stokes component at 1174 nm. The output beam maintains the diffraction-limited spatial profile, while the pulse-duration gets somewhat shorten to about 6-ps. As much as 3 W of the amplified 1174-nm radiation is achieved, when full laser power is used to pump the Raman crystal. No degradation to the mode quality and/or pulse duration is observed in this high power regime. Multiple harmonics are routinely generated in proper nonlinear crystals giving rise to a discretely tunable light source in near-IR, visible, UV and deep-UV.

4. SRS photoacoustic imaging

In the previous set of experiments, when the maximum pump is used, we observe that the residual energy, indeed, goes into acoustic waves generated inside the crystal. We further tested the hypothesis by detecting vibrational-absorption-based photoacoustic signals in D₂O. A glass tube filled with D₂O was placed inside a tank that was filled with de-ionized H₂O (Fig. 5). The tube has an inner diameter of 0.25 mm and an outer diameter of 0.75 mm. Such phantom was built because both D₂O and H₂O have weak linear optical absorptions within the visible and near-IR spectral ranges. Thus, we can achieve a minimal background in PA detection due to linear optical absorption.

The schematic of the experimental setup is shown in Fig. 5. Laser light out of the pump laser (IS8II-E, EdgeWave GmbH; pulse duration: 6 ns; optical wavelength: 523 nm) was routed to mix with the output of the dye laser (Cobra, Sirah Laser and Plasmachnik GmbH; optical wavelength: 601 nm). The optical wavelength of the dye laser was chosen in the way that the

frequency difference matches the Raman lines of D₂O (2370 cm⁻¹ and 2500 cm⁻¹) [18]. The pathlengths of the two laser pulses were adjusted to be identical. The mixed light was focused onto the glass tube by an achromatic doublet lens. The focused beam had a beam diameter of 0.1 mm. The generated PA waves were detected by a high-sensitivity immersion ultrasonic detector (V312-SM, Olympus NDT; center frequency: 10 MHz; Bandwidth: 80%). The detected photoacoustic signals were amplified by a wide-band amplifier (ZFL500LN, Mini-Circuits) for 28 dB and were then digitized by a digital oscilloscope (TDS5034B, Tektronix) at a sampling rate of 250 MS/s.

Only 1D time-resolved photoacoustic signals were measured. First, we measured the photoacoustic signal when the light with both wavelengths was illuminating (denoted as PA_B). Then we blocked the laser light from one of the beams to acquire photoacoustic signals generated from a single optical wavelength illumination (denoted as PA_{op} and PA_{os} , respectively). No signal averaging was performed but high-frequency noise above 120 MHz was digitally filtered. The summation of the PA_{op} and PA_{os} was compared with the PA_B to see if there was any difference in the signal amplitude.

As shown in Fig. 6, the amplitude for PA_B is clearly stronger than that of the $PA_{op}+PA_{os}$ with amplitude increase of more than 40%. This result indicated that certain energy other than the direct summation of the two linear optical absorptions contributed to the amplitude increase in PA_B . Similar measurements and comparisons were conducted several times and PA_B consistently demonstrated an increase in its signal amplitude. Due to the nature of photoacoustic signal generation (induced by optical absorption), such an increase in signal amplitude in PA_B mostly likely resulted from vibrational absorption.

A relatively weak signal is attributed to several factors. Firstly, the Raman cross-section of the heavy water is relatively small and the linewidth of this Raman transition is rather broad. Secondly, Raman photoacoustic excitation is a nonlinear optical process, whose intensity is greatly enhanced when short laser pulses of higher intensity are used. In the subsequent experiment (see [8] for details), we utilized picosecond pulse excitation and used a glass tube filled with chloroform, which has a much stronger Raman cross-section and a narrow linewidth, to achieve high signal-noise imaging of a microscopic object.

5. Conclusion

In this report we demonstrated for the first time applications of stimulated Raman scattering to achieve high efficiency amplification of near transform-limited picosecond pulses at MHz repetition rate and to accomplish chemically selective photoacoustic imaging. The later nicely complements a recently developed SRS microscopy, since Raman photoacoustics provides with a way of imaging objects at the depth 10–100 times larger than those available through optical imaging.

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Figure 1.
Schematic energy diagram illustrating the process of stimulated Raman scattering.

Figure 2.
Schematic of the experimental set-up used for efficient Raman amplification at MHz repetition rate.

Figure 3.

Raman loss spectra of YVO_4 for different polarizations of the input pump and Stokes beams with respect to the crystal orientation. A broadband pulse is used as the pump wave, and a narrowband ($\lambda_2 = 1064 \text{ nm}$) as the Stokes wave.

Figure 4. Supercontinuum generation in Ge-doped fiber. Input energy - $1 \mu J$, output energy - $0.6 \mu J$.

Figure 5.
Experimental setup for Raman photoacoustic imaging using nanosecond pulse excitation.

Figure 6.
Comparison of the photoacoustic signals from the simultaneous illumination of two pump wavelengths and the summation of two individual illuminations.