HIGHLY TUNABLE BROADBAND STIMULATED RAMAN SPECTROSCOPY

SUMMARY: We employ Kerr-instability amplification for broadband stimulated Raman spectroscopy, resulting in a tunable probe from -6000 to 0 cm^{-1} that we use to measure 1-decanol. Our approach provides a broader and more tunable alternative to optical parametric amplifiers.

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Molecular vibrations occur on the femtosecond (1 fs = 1 x 10^{-15} s) timescale. As a result, it can be advantageous to use ultrafast light sources for vibrational spectroscopy. In most cases, the vibrational structure of a molecule can be accessed via its Raman active modes. Femtosecond stimulated Raman spectroscopy (FSRS) is a popular technique for measuring Raman spectra on the femtosecond timescale, providing numerous improvements upon traditional spontaneous Raman spectroscopy [1]. One advantage of using ultrashort pulses is that they have inherently broad spectra. In FSRS, the spectral region of detection is dictated by the bandwidth of the Raman probe spectrum. As such, recent advancements in FSRS have been aimed at improving the bandwidth and tunability of the Raman probe spectrum [1].

The earliest method for generating the Raman probe spectrum was supercontinuum generation (SC). Our method directly amplifies a supercontinuum spectrum to provide higher intensities than possible from simply SC. A more intense Raman probe pulse leads to more stimulated Raman scattering and therefore a greater signal. Later, it became common to use optical parametric amplifiers, but these are limited to bandwidths of around 1200 cm^{-1} due to gain narrowing. More recently, non-degenerate four-wave mixing has been used to create a more tunable and broadband source via multiple beamlets each spanning 1600 cm^{-1}, with a total spectral range of 4000 cm^{-1} [2]. In comparison, our method generates a spectrum from a single beam that spans 6000 cm^{-1}.

Using Kerr-instability amplification (KIA), we first generate a supercontinuum spectrum in sapphire. We then mix the supercontinuum with an intense pump beam in a piece of MgO to directly amplify the supercontinuum by 2-3 orders of magnitude [3-5]. The amplified spectrum is readily tuned via the relative temporal delay of the pump and the so-called (supercontinuum) seed. The amplified spectrum is used as the Raman probe spectrum for our stimulated Raman experiment, resulting in a broad and highly tunable spectrum. We use our novel method to measure the stimulated Raman loss spectrum of 1-decanol by using an anti-Stokes probe pulse. This article is an overview of our recent work on KIA and using KIA as a source for spectroscopy [3-6].

SETUP

Figure 1 outlines our experimental setup. We split the output of our Ti:Sapphire laser into three main arms serving as the KIA pump, KIA seed, and Raman pump. The KIA component of the experiment is indicated by the shaded region. The amplified supercontinuum spectrum, shown by the yellow-green beam, is used as the Raman probe. The Raman pump is modulated by a chopper that is synchronized with the laser and the spectrometer. The Raman pump and probe overlap in a 4 cm cuvette to generate the stimulated Raman response. We measure the stimulated Raman loss spectrum with an Ocean Optics Flame-S spectrometer.

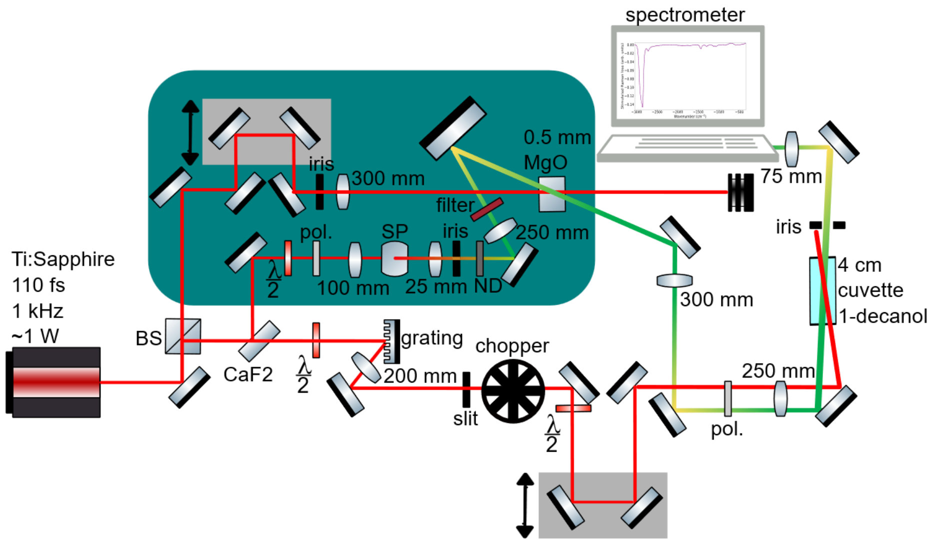

Figure 1. Experimental setup. The shaded region is the setup for KIA, which produces the Raman probe. The Raman pump pulse is created by limiting the laser spectrum via a grating and a slit. We measure the stimulated Raman loss spectrum with an Ocean Optics Flame-S spectrometer. Note: a version of this figure is featured in [4].

RESULTS

Figure 2 illustrates how KIA amplifies the supercontinuum spectrum that is first generated in sapphire. While the un-amplified supercontinuum spectrum is intense enough near the pump wavelength, this intensity drops off quickly in the visible. By amplifying the spectrum using KIA, we have sufficient

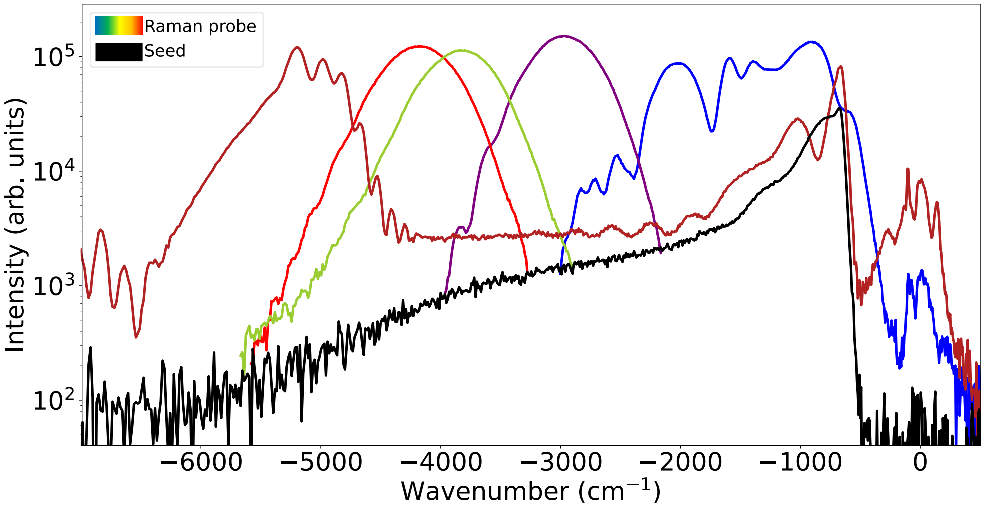

Figure 2. The black line shows the supercontinuum spectrum generated by sapphire. The various coloured lines indicate the amplified spectrum from KIA, the Raman probe spectrum, at different temporal delays between the KIA pump and seed.

Raman probe intensity from -6000 cm^{-1} to 0 cm^{-1}. While adjusting the delay between the KIA pump and seed can optimize amplification at a given wavelength, shown by the coloured lines, there is sufficient intensity to generate the complete Raman loss spectrum even if the delay is tuned to optimize -6000 cm^{-1}. The -594 cm^{-1} (750 nm) cutoff filter attenuates the seed spectrum prior to amplification, but without the filter, KIA can amplify to 2800 cm^{-1} on the Stokes side of the pump. We have chosen to use a filter to optimize amplification on the anti-Stokes side. We choose to operate in the anti-Stokes regime because the main peak shown in Figure 3 is at the limit of our spectrometer if detected on the Stokes side with a wavelength of approximately 1000 nm.

Figure 3 shows the stimulated Raman loss spectrum of 1-decanol. We measure Raman loss rather than Raman gain simply because we operate in the anti-Stokes regime. The main figure highlights the strongest peak near -2900 cm^{-1}, which corresponds to the $\mathrm{CH_2}$ and $\mathrm{CH_3}$ stretching modes, along with an overtone mode at -2858 cm^{-1} which is the exact value of the peak tip. Therefore, it is likely that we are exciting the molecule to the second excited state and driving the methyl stretching modes. The shoulder feature on the main peak at -2720 cm^{-1} indicates a combination mode. Zooming in on the same figure, the inset shows additional weaker Raman modes ranging from -1500 cm^{-1} to -1000 cm^{-1}. In order from left to right, we observe: -1440 cm^{-1} ($\mathrm{CH_2}$ scissoring), -1296 cm^{-1} ($\mathrm{CH_2}$ wagging), -1116 cm^{-1} (likely $\mathrm{CH_3}$ rocking), and -1068 cm^{-1} which could be the CC stretching, CO stretching, or $\mathrm{CH_2}$ rocking mode [7].

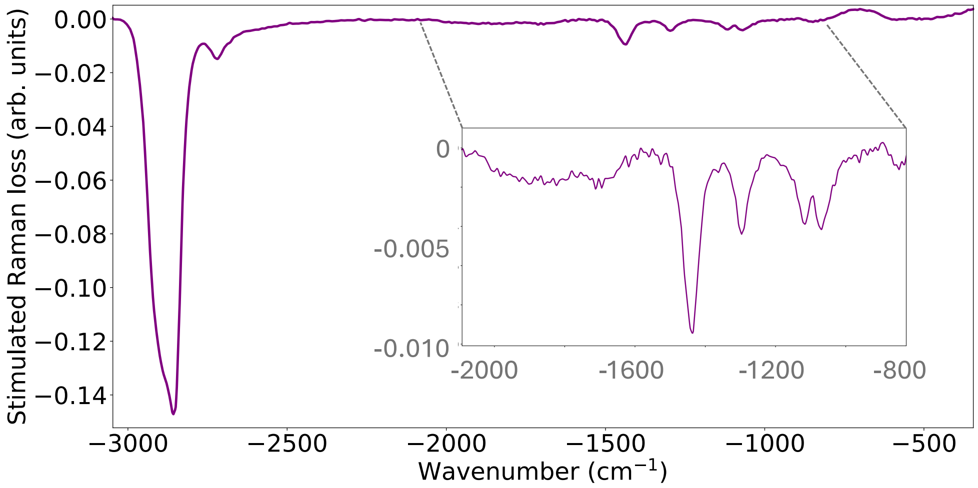

Figure 3. Stimulated Raman loss spectrum of 1-decanol. Shown are the overtone mode at -2858 cm^{-1}, the CH_2 and CH_3 stretching modes ranging from 2880 to 2957 cm^{-1}, and the combination mode at - 2720 cm^{-1}. The inset shows that by zooming-in near -1500 cm^{-1}, we can resolve additional known Raman modes at lower energies [7].

CONCLUSION

Our work aligns with recent advancements in the field of broadband stimulated Raman spectroscopy and introduces a novel technique for generating a broad and tunable Raman probe spectrum. By using Kerr-instability amplification to generate the probe spectrum, we can tune the bandwidth by over 6000 cm^{-1}, demonstrating a broader and more tunable alternative to OPAs. We use our technique to measure the stimulated Raman loss spectrum of 1-decanol.

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