Vibrational energy levels of molecules provide an intrinsic contrast mechanism that can be exploited for spectroscopic identification. Raman spectroscopy based on spontaneous Raman scattering is appealing due to its simplicity and readily interpretable spectra, but suffers from low sensitivity [1]. Coherent Raman scattering (CRS) techniques allow for significantly higher sensitivity due to larger cross-sections and forward scattering. As a result, CRS spectroscopy schemes have been extensively studied over the past two decades. Until recently the dominant CRS spectroscopy technique has been coherent anti-Stokes Raman scattering (CARS). In the past several years, a different CRS process, stimulated Raman scattering (SRS), has proven suitable for high-sensitivity microscopy applications as well [2,3].

In the common CARS and SRS schemes, a picosecond pump beam with frequency $\omega_p$ and a picosecond Stokes beam with frequency $\omega_s$ are focused onto the sample. When the beat frequency $\omega_p - \omega_s$ matches a molecular vibrational frequency, $\omega_{vib}$, third-order nonlinear polarizations are resonantly induced. The polarizations act as sources of coherent fields at distinct frequencies that are blue or red shifted by the vibration frequencies. These act as sources of coherent fields at distinct frequencies that are blue or red shifted by the vibration frequency $\omega_{vib}$. The vibrational spectrum is resolved by examining the amplitude features formed in the spectrum after interaction with the sample. Using this technique, low frequency Raman lines (<100 cm$^{-1}$) are resolved in a straightforward manner.

\[ I_{total} = |E_{in} + E_{nr} + E_r|^2 \]
\[ \cong I_{in} + 2|E_{in}||E_{nr}| \cos \phi_{nr} + 2|E_{in}||E_r| \cos \phi_r \]

Where $E_{in}$ is the input electric field, $E_{nr}$ and $E_r$ are the third order non-resonant and resonant electric field responses respectively, and $\phi_{nr}$ and $\phi_r$ are their phases with respect to $E_{in}$. The approximation in Eq. (1) is valid in the perturbative limit commonly used in spectroscopy, where $|E_{in}| \gg |E_{r}|, |E_{nr}|$. The benefit of interference with the input field is two-fold. First, as $E_{in}$ and $E_{nr}$ are in quadrature, the corresponding interference term vanishes (cos $\phi_{nr} = 0$). Second, $E_{in}$ and $E_r$, which are not in quadrature, coherently interfere. Thus, the resonant signal detected in practice corresponds to the third term in Eq. (1). This results in heterodyne amplification of $E_r$, much like in heterodyne CARS schemes [4]. The large background due to the input field (first term in Eq. (1)) is avoided by modulating either the pump or Stokes beams and measuring the output spectrum using lock-in techniques [2]. In accordance with theoretical analysis, previous SRS work has shown to provide high-sensitivity and display negligible non-resonant background, enabling the successful performance both in narrow-band [3] and multiplex schemes [5]. However, these schemes make use of multi-beam configurations that require maintaining spatial and temporal overlap of the beams and thus a complex experimental setup. Development of a simpler SRS spectroscopy scheme can facilitate the integration of SRS into practical biomedical use.

Here we propose an SRS scheme in which full spectral information can be retrieved with the use of a single femtosecond pulse. In analogy to single-pulse CARS schemes [6,7], the use of a spectrally broadband pulse provides both the pump and Stokes frequencies necessary for excitation of a vibrational mode. Hence, the excitation is caused by all the frequency pairs in the pulse.
with differences that match the vibration frequency of the molecule. For the case of a transform-limited pulse, the dynamics of the system can be thought of as analogous to the multi-beam case, where the excitation of the Raman mode imposes spectral sidebands on the pulse spectrum. The resulting $E_T(\omega)$, for a pulse of an initial central frequency $\omega_0$, has two components: a spectral replica of the incoming pulse blue-shifted to a central frequency $\omega_0 + \omega_{\text{vb}}$ (the anti-Stokes component) and another spectral replica red-shifted to a central frequency $\omega_0 - \omega_{\text{vb}}$ (the Stokes component). Due to the line shape of the molecular resonance, the Stokes and anti-Stokes components are also phase-shifted with respect to the incoming field. The phase-shift of the Stokes component results in positive $\cos \phi_r$ values corresponding to stimulated Raman gain (red dotted line in Fig. 1(b)). The phase-shift of the anti-Stokes component results in negative $\cos \phi_r$ values corresponding to stimulated Raman loss (blue dotted line in Fig. 1(b)). For a broadband transform limited pulse, the overall process results in a red-shift of the central frequency, making it hard to resolve the vibrational spectrum (solid purple line in Fig. 1(b)).

One possible method of regaining chemical specificity is to instill a spectrally-narrow feature in the pulse that will clearly mark the shifted position of the Stokes and anti-Stokes components. Such a feature can be created by inducing a $\pi$ phase-shift in a narrow band of frequencies in the input pulse spectrum using spectral shaping as shown is Fig. 1(c) (this phase pattern will be referred to as $\pi$ phase gate). The phase-shift reverses the gain/loss properties of a narrow frequency band in the shifted spectral replicas while hardly affecting the excitation of the vibrational mode. This results in distinct, spectrally-narrow features in the measured output spectrum that reveal the amount of frequency shift for each Raman line (solid purple line in Fig. 1(c)). Alternatively, the effect of the $\pi$ phase gate can be considered in the time domain. The spectrally-narrow feature created by shaping in the frequency domain corresponds to a temporally-broad pulse in the time domain. The temporally-broad pulse probes the Raman level which was impulsively excited by the unshaped part of the pulse. Thus, the SPSRS scheme resembles the above mentioned multiplex SRS schemes.

To demonstrate single-pulse stimulated Raman scattering spectroscopy, we measured the Raman spectra of several samples. The experimental setup consisted of an amplified Ti:sapphire laser emitting $\sim$30fs pulses centered at 795nm (corresponding to a bandwidth of $\sim$50nm), a programmable pulse-shaper based on a spatial-light modulator (SLM) and a spectrometer (see Fig. 1(d)). The pulses were of varying energies in the range 100nJ - 1\mu J at a 1KHz repetition rate. In order to eliminate the constant input pulse background (first term in Eq. (1)), which is several orders of magnitude larger than the resonant signal, we conducted a differential measurement. The measurement was performed by comparing the spectra of the light emerging from the sample for two slightly different spectral locations of the $\pi$ phase gate. When subtracting the two, not only does the constant input-pulse background vanish but also the broad gain/loss pattern caused by the unshaped parts of the pulse spectrum (see figures 1(b) and (c)). Therefore for frequencies smaller than $\omega_0$, example, where a transform-limited pulse would induce loss, each Raman line is manifested as a narrow peak (loss converted to gain) and dip (subtracted peak) spectral feature on a rather flat background.

High-resolution Raman spectra of several materials are presented in Fig. 2. The measured spectra are in good agreement with the known vibrational spectra of these materials. The Raman lines can be easily identified either on the Stokes (Raman gain) or the anti-Stokes side (Raman loss), allowing for flexibility in the experimental setup. We note that some of the resonant features slightly deviate from the expected peak-dip shape. This is the result of self-phase modulation acquired through propagation in the thick sample (1cm) we used. Nevertheless clear spectral features are visible enabling spectroscopic identification. The demonstrated resolution is 20cm$^{-1}$, limited by the resolution of the SLM which dictates the minimal spectral width of the phase gate that can be applied. Due to the simplicity of the measurement scheme, there is no need to filter out the excitation light. This is in contrast to many other filter-based Raman spectroscopy methods, in which the transition
The width of the filter is what limits the smallest Raman shift that can be measured. Consequently, low-frequency vibrational lines can be measured in a straightforward manner. As seen in Fig. 2(d), several low lines of Sulfur at 217, 152 and 83 cm$^{-1}$ are easily discerned and a feature indicating the 51 cm$^{-1}$ is noticeable on the Stokes side, all in agreement with previous work [10]. Generally, the lowest line that can be detected using this scheme is limited by the spectral width of the $\pi$ phase gate. However, in thick samples, propagation-related effects can cause spectral changes in the vicinity of the $\pi$ phase gate [9] and impose a higher bound on the lowest detectable line, as in the Fig. 2(d).

Another advantageous feature of SPSRS over conventional picosecond SRS arises when the desired goal is detection of a predetermined substance. When applying several $\pi$ phase gates to the spectrum spaced by the differences between the vibrational frequencies of the molecule, the peak-dip features from all the gates are generated at the same frequency. Due to the coherent nature of the process, the signals coherently combine to create a single larger spectral feature. This feature indicates the level of correlation between the measured spectrum and the known spectrum of a substance [11]. The benefits are enhanced signal-to-noise ratio (SNR) compared to each single line, as well as elimination of the need for post-processing of the spectrum. The ability to coherently add lines using SPSRS is demonstrated in the spectrum of carbon tetrachloride, as shown in Fig. 3. The single-phase spectrum Fig. 3(a) reveals two resonant lines which create features at 793nm and 799nm. In the double-gated spectrum shown in Fig. 3(b) the two features are combined at 799nm. The combined feature has a peak-to-dip difference that nearly equals (90%) the sum of the two individual lines, representing an appreciable enhancement of the SNR. The feature can be further enlarged by optimizing the relative phase of the gates and their spectral locations either manually or through the use of an adaptive algorithm [11].

In conclusion, we have demonstrated vibrational spectra acquisition using a single-pulse SRS scheme. Spectral shaping enables full control over the interference of the input field and the generated resonant electric field, facilitating the creation of narrow spectral features that indicate the frequencies of the Raman lines. Using this method, all vibrational levels within the detection range can be simultaneously identified in a similar fashion to multiplex SRS schemes but with a single beam setup. Two unique features of the SPSRS scheme have been demonstrated, the ability to distinguish low-lying Raman lines and the ability to coherently add the signal from several lines for an improved spectroscopic fingerprint. Spectroscopy of low-lying Raman lines is a useful tool in various research fields. Examples include monitoring electrically distinct carbon nanotubes [12] as well as studying the hydration dynamics of DNA films [13]. Furthermore, by employing fast shaping techniques together with lock-in detection [14] the sensitivity of our setup can be substantially increased and SPSRS can become an attractive scheme for microscopy and biological imaging.

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