9. Coherent Control in CARS

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9.1 Introduction

In CARS spectroscopy pump and Stokes photons at frequencies $\omega_p$ and $\omega_s$, respectively, coherently excite molecular vibration at the frequency $\Omega_{\text{vib}} = \omega_p - \omega_s$, and the vibration is subsequently probed by interaction with probe photons at frequency $\omega_{pr}$. The vibrational spectrum is resolved by measuring the blue shift of the generated anti-Stokes photons frequency from the probe frequency $\omega_{AS} = \omega_{pr} + \Omega_{\text{vib}}$. CARS spectroscopy is typically performed as a multi-beam, multi-source technique [1–3] (Figure 9.1a and b), which is experimentally challenging to implement due to the strict requirement of spatial and temporal overlap of the excitation beams. This paradigm has changed with the utilization of quantum coherent
control and pulse-shaping techniques in CARS spectroscopy. In brief, the goal of quantum control is to drive a quantum system from an initial state to a desired final state by exploiting constructive quantum-mechanical interferences that build up that state amplitude, while avoiding undesirable final states through destructive interferences [4]. This approach can be directly applied in CARS spectroscopy to selectively excite a single vibrational level of a specific chemical species, while minimizing the excitation of undesirable levels or species (Figure 9.1c). Today, the most common experimental approach to quantum control uses shaped femtosecond pulses. To effectively exploit quantum
interferences, one must preserve the quantum-mechanical phase and hence avoid decoherence. It is therefore advantageous to use ultrafast interactions that are faster than the lifetimes of the relevant levels or, in equivalent terms, to use laser pulses that are spectrally broader than the width of those levels. This is in contrast with classical laser spectroscopy, where the desired laser line width is traditionally much narrower than the width (and spacing) of the level(s) being assessed (e.g., Figure 9.1a). The most common route to coherent control utilizes the technique of femtosecond pulse shaping. For control, one can apply a sequence of femtosecond pulses to drive the system impulsively, but the most versatile approach uses an optical setup known as a pulse shaper [5] in which the short pulses are modified to generate more complex, specifically tailored pulses by controlling the individual frequencies of the short pulse. The most common experimental configuration for pulse shaping is based on spatial dispersion and is often referred to as a 4-f pulse shaper, which closely resembles a back-to-back optical grating spectrometer (Figure 9.2). The first grating disperses the spectral components of the pulse in space, and the second grating packs them back together, while a pixelated spatial light modulator (SLM) applies a specified transfer function, thereby modifying the amplitudes, phases, or polarization states of the various spectral components. In essence, the shaper is an optical synthesizer that can generate complex pulses with a temporal resolution limited by the inverse of the spectral content of the pulse and a maximal controlled duration limited by the spectral resolution of the setup and the SLM pixel size. The configuration shown in Figure 9.2 is just one approach to pulse shaping, and a few other techniques have been employed, most notably an acousto-optical device known as the dazzler [6].

Utilizing pulse shaping, CARS spectroscopy can be converted from a multi-source, multi-beam technique to a single-source, single-beam technique, which employs a single femtosecond pulse for CARS spectroscopy and microscopy [7–10]. In such “single-pulse” schemes, a single wideband femtosecond pulse simultaneously provides the necessary pump, Stokes, and probe photons, and spectral selectivity is attained by pulse shaping (Figure 9.1c and d). Femtosecond single-pulse CARS techniques are attractive as only a single laser source is required and the spatiotemporal overlap of the pump, Stokes, and probe photons is inherently maintained. Moreover, because of their high peak intensity, femtosecond pulses are favorable over picosecond pulses for a variety of other nonlinear.

FIGURE 9.2  Schematic drawing of a Fourier-domain 4-f femtosecond pulse shaper. A transform-limited input pulse is dispersed by the input grating (left), and the different frequency components are modified by the mask function at the spectral plane using an SLM. The different spectral components are then recombined by the output grating (right) to form the shaped output pulse.
processes such as second- and third-harmonic generation (SHG, THG) and multiphoton fluorescence, an advantage for label-free multimodal microscopy [11]. Since first demonstrated [7], single-pulse CARS schemes have been utilized for vibrational imaging [12,13], time-resolved chemical microanalysis [14], and remote detection of hazardous materials [15,16]. The two main difficulties when implementing CARS using femtosecond pulses are the loss of spectral resolution and an increase of non-resonant contribution. First, the loss of spectral resolution is the result of the pulse bandwidth being much broader than the width and spacing of vibrational lines [7,17]. This can be intuitively portrayed as the entire pulse bandwidth serving as a probe. Second, the non-resonant contribution is significantly enhanced due to higher peak powers, compared to longer pulses of equivalent energy, and the inherent temporal overlap of the pump, Stokes, and probe photons. While both of these complications severely inhibit the use of unshaped femtosecond pulses in CARS, the use of pulse-shaping techniques can easily address them. Specifically, through careful pulse shaping, a spectroscopic resolution orders of magnitude better than the pulse bandwidth can be retained, and the non-resonant background can be reduced or strategically used as a local oscillator for signal amplification.

In this chapter, we review the different pulse-shaping schemes for femtosecond and single-pulse CARS. In particular we evaluate the effect of specific pulse shapes in terms of driving and probing molecular vibrations. Figure 9.1 briefly summarizes the main approaches for femtosecond single-pulse CARS, together with the corresponding conventional multi-beam analogs. The various different pulse-shaping schemes can be divided into two main approaches. In one approach, pulse shaping is used to gain control over the vibrational Raman excitation process (Figure 9.1c). Tailoring the pulse allows exciting selectively a single vibrational level instead of the multiple levels that would have been excited by an unshaped wideband pulse [7]. Different pulse shapes are then used to excite different vibrational levels, in the same manner that different pump and Stokes frequency pairs are used in conventional multi-beam CARS (Figure 9.1a). This is achieved by altering the excitation probability amplitude of a particular Raman mode $A(\Omega_{\text{ vib}})$ (Equation 9.1):

$$A(\Omega) = \int d\omega E^*(\omega)E(\omega - \Omega) = \int d\omega |E(\omega)|\left|E(\omega - \Omega)\right| e^{i\phi(\omega) - \phi(\omega - \Omega)}$$  (9.1)

$A(\Omega)$ is the probability amplitude to populate a vibrational level with energy $\Omega$ via Raman excitation, function of the incident pulse electric field spectral amplitude $E(\omega)$ [10]. The population amplitude $A(\Omega)$ is the sum of all possible two-photon pairs leading to the same intermediate state and can be controlled by shaping the spectral phase of the incident electric field, $\phi(\omega)$ (Figure 9.1c). The term $E(\omega)$ describes the pump field and the term $E(\omega - \Omega)$ is the Stokes field, both originating from the same wideband ultrashort pulse. In an alternative approach, pulse shaping is used to control the probing process (Figure 9.1d). By spectral phase, amplitude, or polarization shaping of a narrow frequency band, a narrowband probe can be defined in the wide pulse bandwidth, allowing for multiplex single-shot measurement of the vibrational spectrum [8,9,18,19] (Figure 9.1d). This is analogous to conventional multiplex CARS [1,8,9], where several
vibrational levels are coherently excited by broadband pump and Stokes beams, and is subsequently probed by a narrowband probe beam, producing blue-shifted spectral peaks in the CARS spectrum (Figure 9.1b). In multiplex single-pulse CARS, the shaped narrowband probe produces narrow spectral interference features in the CARS spectrum, which are also blue-shifted from the shaped probe frequency by the molecular vibrational frequencies (Figure 9.1d). The interference features are due to the dependence of the resonant signal on spectral phase compared to the non-resonant signal (Equations 9.2 and 9.3). The vibrational spectrum is easily resolved by measuring the energy shift of these features from the probe frequency. An advantageous coherent-control feature of this approach is accessible by shaping multiple probes. A large coherent interference signal from contributions of several vibrational levels can be generated by shaping several probes spaced by the vibrational lines of a known substance. This produces an anti-Stokes signal that is tailored to a specific chemical species and is significantly larger than the linear sum of each individual vibrational contribution [20]:

\[
P_{r}^{(3)}(\omega) = C_r \int_{0}^{\infty} d\Omega \frac{1}{\Omega - \Omega_{R} - i\Gamma_{R}} E(\omega - \Omega)A(\Omega)
\]

(9.2)

\[P_r(\omega)\] is the nonlinearly induced vibrationally resonant polarization, in a CARS process, from a single vibrational level, using a broadband pulse [10]. This polarization generates the measured electric fields at the anti-Stokes frequencies. \(\Omega_{R}\) and \(\Gamma_{R}\) are the Raman level frequency and line width, respectively, and \(A(\Omega)\) is the probability amplitude to populate a vibrational level with energy \(\Omega\) via Raman excitation (Equation 9.1). \(C\) is a constant which includes the summation over the dipole moments. \(E(\omega - \Omega)\) in equation is the probing field:

\[
P_{nr}^{(3)}(\omega) = C_{nr} \int_{0}^{\infty} d\Omega \frac{1}{\Omega} E(\omega - \Omega)A(\Omega)
\]

(9.3)

\[P_{nr}(\omega)\] is the nonlinearly induced non-resonant polarization in a CARS four-wave-mixing process with a broadband pulse. The term \(1/\Omega\) is a correction term accounting for the not fully instantaneous nature of the non-resonant process [10].

Although intuitively depicted in the frequency domain, the different single-pulse CARS approaches can be also simply portrayed in the time domain (Figure 9.1c and d, right column): In the selective excitation schemes, the tailored pulse shapes are manifested in the time domain by a train of two or more impulses, which maximize the excitation for the vibrational frequency with the period equal to the pulse separation, in a similar manner to pushing a resonant swing (Figure 9.1c). In the narrow spectral probing schemes, the narrow spectral phase-, amplitude-, or polarization-shaped probe is manifested in the time domain as a temporally extended probing pulse at the shaped wavelength. The overall outcome of such shaping in the time domain is an impulsive femtosecond excitation of coherent molecular motion by a femtosecond pulse, followed by narrowband probing with a much longer pulse (typically hundreds of femtoseconds to picoseconds). The resulting vibrational features in the CARS spectrum are the
coherent interference of the CARS field induced by the time-extended probe and the non-resonant-dominated four-wave mixing field induced by the unshaped part of the excitation pulse. For a single shaped probe, the optimal probe pulse duration and delay are set by shaping a “matched-filter” probing with spectral width equal to the vibrational line width [21,22].

It is important to note that pulse shaping for femtosecond CARS does not necessarily require a programmable dynamic pulse shaper, which is typically a relatively complex and costly experimental setup, which requires careful calibration [5]. Selective excitation (Figure 9.1c) can be attained by spectral focusing of two chirped femtosecond pulses [22-24] or double-pulse excitation [25,26], albeit these schemes rely on a multi-beam experimental apparatus in contrast to the single beam used in the pulse-shaper-based techniques. Narrow probing (Figure 9.1d) can be attained by shaping a narrowband probe using simple notch filters [18], Fabry-Perot interferometers and even a thin wire in the spectral plane of a pulse compressor [19], a common apparatus in amplified femtosecond sources.

This chapter is organized as follows. The two major approaches, to obtain multiplexed measurements via probe control or through selective excitation, are discussed separately. In both approaches, the progression from conventional multi-beam experiments is briefly discussed with the progression to single-pulse experiments that employ coherent control. The major discussion points of the multiplexed techniques include methods for removing the non-resonant contribution from the CARS signal, alternative probe shaping techniques that are not based on the standard 4-f shaper design, and applications of single-pulse, multiplexed CARS. The major discussion points of the selective excitation techniques include alternative shaping functions for greater mode selectivity, alternative excitation sources for increasing the detectable Raman bandwidth, heterodyne amplification for enhanced sensitivity, two-color configurations with independent probe shaping for multi-octave frequency range, and fast pulse shaping techniques for rapid detection of selectively excited Raman levels.

9.2 Multiplexed Measurements with Probe Control

9.2.1 Multi-Beam Multiplexed CARS

Using a combination of both narrowband and broadband pulses, one can achieve multiplexed CARS measurements [25,27,28]. This is conventionally implemented with a broadband Stokes, typically through supercontinuum generation, and a narrowband pump, which also serves as a probe. In this configuration (Figure 9.1b), the pump and Stokes beams simultaneously drive molecular vibrations of multiple levels ($\Omega_R$). Following vibrational excitation, the levels are interrogated by a narrow probe, which inherently dictates the spectral resolution. The resulting CARS spectrum, accordingly, contains features from all the excited Raman modes at spectral locations corresponding to energy shifts from the probe frequency.

Multiplexed CARS measurements are also possible using broadband, femtosecond pulses exclusively by employing pulse-shaping techniques. In a multi-beam experiment, Oron et al. used transform-limited pump and Stokes beams to drive molecular vibrations and probed with a shaped beam to obtain spectral resolution one order
of magnitude better than the probe bandwidth [29]. Specifically, it was shown that a probe shaped with a phase step can be used to coherently sum off-resonant quantum paths driving molecular vibrations above and below the resonant frequency (Figure 9.3). While still applying multiple laser sources, this work was the first to use pulse shaping and phase control as a tool for spectroscopy, and in particular as a mean to enhance spectral resolution.

The concept of shaping the probe beam with a phase step is based on the inherent phase inversion at the resonance of driven harmonic systems. As seen in Equation 9.2, while the numerator of the resonant polarization is real and positive, the denominator term \((\omega - \Omega) + i\Gamma\) inverts the phase over a range of \(\Gamma\) about the resonant frequency \(\omega_r\). Such systems are driven in phase with the driving force below the resonant frequency, in quadrature at the resonance, and inversely above it. Consequently, when probed with a transform-limited probe, destructive interference is induced between pathways leading to driving fields above and below the resonant frequency. By applying probe phase function of \(\Phi = \arctan[(\omega - \omega_r)/\Gamma]\) (Figure 9.3), one can achieve an enhancement in the CARS signal at a given frequency \(\Phi\) in the presence of a Raman level due to constructive interference of off-resonant terms [29]. While the applied phase inverts the relative sign of the frequencies much above and below \(\omega - \omega_r\), nearly linear phase is added to the frequencies in the range of \(\Gamma\) about \(\omega - \omega_r\). The linear phase component introduces a small delay of the probe pulse with respect to the pump and Stokes, which has been shown useful to reduce non-resonant contribution [21,29–32]. More recently, the Offerhaus group has developed a similar multi-beam approach using both negative and positive phase steps to more accurately retrieve spectral line widths. They report a maximum resonant signal when the phase step is on the order of the width of the vibrational resonance [33,34].
9.2.2 Single-Pulse Multiplexed CARS

In a seminal experiment by Oron et al., it was demonstrated that a single pulse can serve to provide the necessary pump, Stokes, and probe photons to obtain multiplexed CARS measurements [8]. In this configuration, a narrow spectral band, encoded with a $\pi$-phase shift ($\pi$-gate), serves as an effective probe for multiplexed CARS (Figure 9.4). This technique takes advantage of the coherent relationship between the resonant and non-resonant signal and utilizes the strong resonant background as a local oscillator in a homodyne amplification scheme. Since the measured CARS signal is the coherent sum of the resonant and non-resonant signal, amplification is maximized when the phase difference is 0 or $\pi$. Encoding a narrow $\pi$-gate in the excitation pulse results in a $\pm\pi/2$ phase shift between the resonant signal and the non-resonant background, which are initially in quadrature. However, similar to the previously discussed multi-beam experiment that shaped a phase step, there is an enhancement of the resonant signal due to the off-resonant contributions as a result of the inherent phase shift of the driven oscillator. Specifically, enhancement occurs at a given frequency $\omega$ in the presence of a resonant signal from a level ($\Omega_R$), generated by a narrowband probe centered at $\omega - \Omega_R$. Since the $\pi$-gate essentially affects the resonant signal as two $\pi$-steps with inverse signs, the resulting resonant spectrum has two features with opposite phase (Figure 9.5). The resulting measured CARS spectrum, that is, interference of the resonant and non-resonant signals, has a peak-dip feature due to the edges of the $\pi$-gate. Since the $\pi$-gate

![Figure 9.4](image_url)

**Figure 9.4** Schematic drawing of single-pulse multiplexed CARS; (a) the excitation pulse spectral intensity (solid black line) and spectral phase of a transform-limited pulse (gray line) and a 10-pixel $\pi$-phase gate pulse (dashed line). (b) Temporal intensity of a transform-limited pulse (gray line) and a $\pi$-phase-gate-shaped pulse (dashed line). (c) Calculated population amplitude $A(\Omega)$ for the transform-limited pulse (gray line) and the shaped pulse (dashed line). (From Dudovich, N. et al., *J. Chem. Phys.*, 118, 9208, 2003. With permission.)
simultaneously probes multiple excited vibrational levels, the resulting spectrum is multiplex with a peak-dip feature corresponding to the various Raman modes.

Although this technique is complimentary to the multi-beam approach (Figure 9.3) where the probe beam is spectrally encoded with a phase step, the single-pulse configuration (Figure 9.4) alternatively employs the use of a narrow phase gate (π-gate). The benefit of using a π-gate is the limited effect on the excitation probability (Figure 9.4c). Since the same pulse provides the pump, Stokes, and probe photons, it is essential to limit the pulse deviance from the transform limit in order to preserve maximal excitation probability \( A(\Omega) \). This method has been shown to yield spectral resolution two orders of magnitude better than the pulse bandwidth [8]. As in the case of the multi-beam phase-step configuration, the resolution of this technique is dependent on the slope of the π-gate rather than the spectral width. Furthermore, this technique is particularly attractive because it relaxes the need to suppress the non-resonant background. By strategically creating resonant features with similar phase to the large non-resonant background, the non-resonant signal can consequently be used to amplify the resonant CARS signal.

Additional methods, based on narrow spectral probing, have been developed to simplify measurements and improve sensitivity. Due to the coherent nature of CARS signals, it is possible to use more advanced probing methods that interact with photons generated from multiple levels. This technique alleviates the need for full spectral acquisition to obtain multiplexed spectra by coherently summing the contribution from multiple levels to a single measured frequency. This method, coined as “all optical processing,” has been demonstrated using multiple probes in a configuration where \( \omega_{AS} = \omega_{p1} + \Omega_1 = \omega_{p2} + \Omega_2 = \cdots = \omega_{pN} + \Omega_N \) where the probes are centered around \( \omega_{pn} \) for each given level \( \Omega_n \) of a target chemical species [20]. Under this condition, the enhanced signal at frequency \( \omega_{AS} \) is due to the coherent contribution from multiple levels (Figure 9.6a and b).

FIGURE 9.5 Comparison of (a) transform-limited and (b) phase-gate-shaped pulses in a single-pulse CARS scheme. The top images show the calculated CARS electric field as a function of frequency for the resonant signal (solid line) and the non-resonant background (dashed line) for Ba(NO\(_3\))\(_2\). Also shown is the relative phase between the two (gray line). The bottom images show the calculated resulting CARS spectrum. (From Dudovich, N. et al., J. Chem. Phys., 118, 9208, 2003. With permission.)
The signal is measured with enhanced sensitivity, compared to a single probe, as the total signal is greater than the linear sum of the individual contributions. This technique is particularly useful when interrogating compounds with overlapping lines. As seen in Figure 9.6c through e, a configuration can be implemented where the CARS signal from a particular level is diminished by destructively interfering with the contribution from a different level. This essentially negates the contribution of a specific Raman mode for a particular compound, while allowing for the detection of another with similar level structure. This method can also prove useful in samples with unknown spectra where a cost function can be satisfied to maximize the signal at a given spectral range while applying numerous probes at various spectral locations [20].

**9.2.3 Techniques for Separating and Eliminating the Non-Resonant CARS Signal**

Although the necessity of removing the non-resonant background is greatly relaxed in homodyne amplification schemes, it is still beneficial for faithful reproduction of Raman spectra. The elimination can be achieved through either experimental technique or computational post-processing. In the former scenario, it has been shown that the non-resonant contribution can be almost entirely eliminated using both phase- and polarization-shaping techniques [9]. By shaping a narrow probe in the pulse bandwidth, at an orthogonal polarization \( P_y \), the ultrafast pulse is essentially broken into two distinct pulses separable by polarization. The resulting resonant spectrum, probed by
the orthogonal polarization, can then be separated from the non-resonant signal at $P_y$. Further suppression of the non-resonant signal can be achieved with the addition of a $\pi$-phase step at the center of the probe spectrum. The phase step splits the probe into two spectrally longer pulses with opposite phase (Figure 9.7a and b), crossing zero intensity at zero delay, where the excitation intensity peaks. Due to the broad spectral response, the non-resonant background from the two probe pulses destructively interfere with a reduction of multiple orders of magnitude, allowing for straightforward detection of the Raman spectrum (Figure 9.7c and d).

Using similar experimental approach, Lim et al. developed a computational technique to extract pure Raman spectra by separating the resonant signal into the corresponding real and imaginary components ($I_{\text{Raman, real}}$, $\text{Im}[I_{\text{CARS}}]$). This is achieved by measuring the CARS signal at polarizations $\pm \pi/2$ from the pump/Stokes beams (also orthogonal to the probe) [35]. By controlling the phase of the probe over few realizations, the real and imaginary parts of the resonant signal can be numerically calculated, and hence, a more accurately represented Raman spectrum can be resolved. This technique has been demonstrated in various samples, and the computed spectra were found to be virtually background free [36]. In an alternative approach, the non-resonant background can be eliminated using a technique referred to as “Fourier transform spectral interferometry” (FTSI-CARS). Unlike the previously described method, FTSI-CARS can be implemented with phase only shaping and is applicable to single-pulse, multiplexed measurements. This technique is based on the causality of CARS process, that is, there is no signal before the laser excitation. In brief, the imaginary and real parts of the resonant signal are separated by zeroing the values at $t < 0$, attained by the Fourier transform of a normalized CARS spectrum [37]. Transforming this causal timetrace back to the frequency domain yields the imaginary part of the spectrum. Contingent on this calculation, it was found that the sum of the amplitude ($|I_{\text{real}}|$) and the imaginary part ($\text{Im}[R_{\text{resonant}}]$) of the resonant signal accurately portrays the Raman vibrational spectrum [12]. It has also been demonstrated that the signal sensitivity can be further improved by 2 orders of magnitude by incorporating amplitude shaping after reduction of the laser repetition rate and optimization of the power, bandwidth, and spectral phase [12].

**FIGURE 9.7** Schematic drawings of a single-pulse CARS scheme, with phase and polarization shaping; (a) spectral and (b) temporal electric field amplitudes in both the $x$ polarization (solid line) and the $y$ polarization (dashed line) for phase- and polarization-shaped excitation pulses. A shift of the spectral phase by $\pi$ (in (a)) is equivalent to a sign inversion of the electric field amplitude in a band within the $y$-polarized component. For convenience, the spectral field amplitude (b) has been normalized. In practice, the peak field amplitude of the $x$-polarized component is an order of magnitude higher than that of the $y$ component. (c) Normalized measured CARS spectrum and (d) the extracted Raman spectrum after background subtraction from p-xylene (resonant at 313, 459, and 830 cm$^{-1}$). (Adapted from Oron, D. et al., *Phys. Rev. Lett.*, 90, 213902, 2003. With permission.)
9.2.4 Alternative Shaping Techniques

One of the drawbacks of commonly employed single-pulse, multiplexed CARS techniques is the need for a pulse-shaping apparatus. Pulse shaping is typically achieved with the use of an SLM in a 4-f configuration [5]. The SLM is costly and requires precise alignment and calibration of wavelength-dependent induced phase. Recently, there have been advances in system configurations that alleviate the need for a pulse shaper entirely. In one such technique, the Milner group demonstrated how multiplexed spectra can be acquired by taking the autocorrelation of the detected CARS signal [38]. As in the previously described configurations, the pulse is shaped, however, randomly in phase and/or amplitude. Since the shaped pulse also acts as a probe, with numerous features, the CARS signal is effectively shaped according to similar features at spectral regions corresponding to the multiple Raman energy shifts. By taking an autocorrelation of the CARS signal, the Raman spectrum, which is convolved with the randomly shaped probe, is revealed with a resolution on the order of the noise correlation length. The only requirement is that the applied phase/amplitude function applied to the pulse is constant over the time required for an autocorrelation. The shaping can be achieved by the use of a random diffuser in the spectral plane or simply passing the pulse through a multimode fiber. In another study, Katz et al. also alleviated the use for a pulse shaper by demonstrating multiplexed measurements employing a narrow notch filter as a spectral amplitude and phase shaping device as shown in Figure 9.8 [18,39]. The spectral shaping

![Figure 9.8](image)

**Figure 9.8** Experimental setup for notch-shaped single-pulse CARS using an RPCS. (a) The optical setup: The wideband excitation pulse (i) is shaped with a tunable narrowband spectral notch by the RPCS filter (ii). The spectral notch serves as a narrow probe for the CARS process generating narrow well-defined features in the CARS spectrum, which are blue-shifted from the probe by the vibrational frequencies (iii). (b) A schematic diagram of the RPCS double grating waveguide and (c) atomic force microscopy measurement. (From Katz, O. et al., *Opt. Express*, 18, 22693, 2010. With permission.)
is achieved using a resonant photonic crystal slab (RPCS) filter, which is a grating waveguide structure comprised of a thin waveguide layer with an etched sub-wavelength grating. While most of the spectrum passes through the filter, a narrow band is coupled into the waveguide and destructively interferes with the pulse. This results in a narrow (<1.5 nm) notch at a central frequency, which is angularly dependent on the incident angle of the excitation beam to the filter (Figure 9.9a). Complimentary measurements can be taken corresponding to slightly different notch locations (Figure 9.9b), and the CARS spectrum can be easily calculated taking into account the non-resonant background and excitation probability (Figure 9.9c). This technique is particularly attractive because any conventional multi-photon microscope setup can be used for CARS measurements provided the pulse bandwidth is wide enough to excite the vibrational levels.

### 9.2.5 Applications of Single-Pulse Multiplexed CARS

Single-pulse, multiplexed CARS measurements have proven to be useful in a host of applications. Notably, the technique of shaping both phase and polarization has been used to measure Raman transitions in gases. It has been shown that spectrally broad (sub-10 fs), single pulses can be shaped to probe lines greater than 2000 cm⁻¹. Particularly, the pressure dependence and percentage of N₂ in mixtures has been characterized [40]. In a similar study, the CO₂ was interrogated with visible Raman peaks at 1285 and 1388 cm⁻¹, corresponding to Fermi dyads [41]. A new realization of standoff chemical detection has also been born from multiplexed CARS using single pulses. With a phase-only shaped spectrum, experiments have been conducted to collect CARS signals at standoff distances greater than 10 m. These experiments demonstrated the ability to collect spectra at a distance from solids, liquids, and gases [15,16,42]. In a standoff, experiment, Katz et al. demonstrated that closely separated Raman lines could be detected at a distance by using a matched frequency filter corresponding to the shape caused by the interference of the phase gate (Figure 9.10) [15]. In a similar study, Natan et al. incorporated the concepts from standoff detection and shaper-free...
configurations; they demonstrated detection of explosive materials from a distance of 50 m using an RPCS filter as a shaping device [43].

Single-pulse multiplexed techniques have also been applied to microscopy. Specifically, Raman spectra were obtained across a 2-D plane, and images were then generated based on the contrast of a specific Raman levels. This has been shown in generating contrast between solids, including PDMS/amide [36] and polystyrene/polyethylene terephthalate [12]. More recently, this technique has been demonstrated using low average powers, less than 30 mW, in liquids and thinly sliced potato sections, where the strong skeletal mode of starch granules was exploited (Figure 9.11) [18]. The ability to successfully obtain images from samples using low intensities is a first step in moving toward single-pulse CARS techniques for biologically relevant applications.

9.3 Time-Domain and Selective Excitation CARS

9.3.1 Multi-Beam Selective Excitation

The earliest applications of sub-100 fs pulses for time-domain measurements of CARS date back to the late 1980s with Leonhardt’s novel experiment measuring molecular quantum beats in liquids [44]. This technique exploits the fact that when molecules are excited to a given Raman level, there is molecular vibration at the frequency corresponding to that particular energy level. The main principle of time-domain approaches is that if one were able to identify at which frequency(s) a molecule is vibrating at, then the complete Raman spectrum can be identified via Fourier transform. One such
A technique for identifying the vibrational frequency components (Raman levels) is by using a series of pulses that provide pump/Stokes photons to excite molecular vibration, and a time-delayed probe pulse. Since a molecule vibrates in time, the probe experiences a time-dependent energy shift, which is due to the oscillating molecular polarization. By taking a series of measurements corresponding to different probe delays from the excitation, the vibrational beat frequencies can be resolved, which are a Fourier-related pair to the time-domain measurement. This technique, coined as “resonant femtosecond CARS,” was originally carried out in a simplistic three-beam configuration and successfully observed vibrational modes of gases [45–47]. However, as the technique evolved, resonant femtosecond CARS benefited from the addition of pulse-shaping techniques and moved toward applications measuring solid materials. Zeidler et al. designed an experiment where a shaped Stokes pulse was used in combination with a delayed, transform-limited probe [48]. Using an iterative feedback algorithm, specific phase-and amplitude-shaping functions were found to selectively enhance the population of specific Raman modes. Continuing with the goal of selective excitation of Raman modes, Oron et al. showed that phase-only encoding of the pump and Stokes beams can lead to selectivity in the excited Raman modes and eliminate the need to scan the probe delay and spectrally resolve the measured signal [30]. This technique was first demonstrated in a three-beam setup using 100 fs second pulses corresponding to a bandwidth...
of 120 cm\(^{-1}\). Particularly, this work showed the advantage of encoding \(\pi\)-phase gates in the pump and Stokes beams with an energy difference (\(\Delta E\)) (Figure 9.12). In the case when \(\Delta E\) corresponds to a vibrational level, an enhancement is observed in the CARS signal. This enhancement is observed because the non-resonant signal is diminished with the application of the \(\pi\)-gates and the vibrational mode is maximally excited when \(\Delta E\) corresponds to the energy level, that is, the excitation photon pairs are in phase (see Equation 9.1). This can be simply thought of as carefully altering the pump and Stokes beams to produce a signal enhancement by constructively interfering with two narrow bands of frequencies with energy differences satisfying the population requirement of a specific energy level. Consequently, by scanning the spectral location of one of the gates, and hence \(\Delta E\), one can interrogate a sample and identify the Raman modes. Since this technique selectively excites a specific Raman mode, a single detector can be used rather than a spectrometer. Although there is a trade-off between spectral resolution (narrowness of the gate) and total enhanced signal (width of the gate), this method can be used to gain spectral resolution two orders of magnitude better than the pulse bandwidth [30]. In this work, it was also shown that there was a benefit to applying a fixed probe delay to further reducing the non-resonant background.

### 9.3.2 Single-Pulse Selective Excitation

The concept of tailoring a single femtosecond pulse to selectively populate and then probe a specific Raman level has been studied intensively. In a pioneering experiment, Dudovich et al. first demonstrated how coherent control techniques can be applied to selectively excite specific vibrational levels and obtain full spectral information [7]. The underlying concept of selective excitation is the application of periodic spectral phase functions to the pulse, a concept that was demonstrated already a decade earlier on molecular crystals [49]. This method can be intuitively reasoned in both the frequency and time domain (Figure 9.13a and b). First, in the frequency domain, a specific vibrational level, \(\Omega\), is populated by a combination of photons with frequencies such that the energy difference \(h\omega_1 - h\omega_2 = \Omega\) with a relative phase \(\phi(\omega) - \phi(\omega - \Omega)\). Therefore, to maximize the population amplitude of a particular vibrational level at a frequency \(\Omega\): \(A(\Omega)\),
the electric fields at frequency pairs separated by the vibrational energy should be in phase to achieve highest constructive interference, that is, $\phi(\omega) = \phi(\omega - \Omega)$ as seen in Equation 9.1. While this condition is satisfied for all levels given a transform-limited pulse, there is selective population of $\Omega = N\Omega_m$ where $N$ is an integer and $\Omega_m$ is the spectral phase modulation period (Figure 9.13c). In simplicity, the periodic phase creates constructive interference between all the various spectral components, which drive a particular molecular vibration while destructively interfering with paths driving other frequencies. This is similar to the previously discussed multi-beam approach where narrow $\pi$-phase gates were encoded into the pump and Stokes beams, separated by the energy corresponding to the desired vibrational level [30].

In the time domain, one can intuitively reason the dynamics of selective excitation by thinking of the induced molecular vibration. As dictated by the Fourier transform, the corresponding effect of a periodic phase is temporal pulse splitting leading to a train of pulses equally separated by $\tau_m = 2\pi/\Omega_m$ (Figure 9.13b). When the period of the modulated phase pattern corresponds to an integer number of the vibrational energy, the temporal delay between the split pulses matches the period (or integer harmonic) of the molecule vibration. When this condition is satisfied, the pulse train coherently drives oscillations at resonant frequencies corresponding to vibrational periods $T = \tau_m/N$ (Figure 9.13c). This can be thought of as coherently driving a mass on a spring with the proper phase at the resonant frequency or periodically pushing a child on a swing such that the push is given at the same point in the motion. While the effect coherently adds energy to the resonant mode, the non-resonant signal has been shown to be reduced by 2 orders of magnitude due to the decrease in peak power as an effect of the temporal pulse splitting [7,10]. It has been shown that the addition of harmonic

![Figure 9.13](image-url)
content in the spectral domain creates a series satellite of pulses in the time domain, which can further reduce the non-resonant background while leaving the resonant term virtually unaffected (Figure 9.14a). When using a just single periodic frequency, one measures a predominantly resonant signal, which is greater than the non-resonant background by a factor of 4 [7]. Using a function with two or four harmonics results in a further attenuation of the non-resonant signal by a factor of ∼80 and ∼250, respectively (Figure 9.14b) [10].

As in the multi-beam approach, the technique of selectively exciting Raman levels using a single-pulse is particularly simple in terms of detection as a single detector can be used, and there is no need to spectrally resolve the CARS spectrum. Moreover, one can identify the Raman spectrum from a given sample by taking measurements of the total CARS signal from realizations corresponding to different pulse separations (Figure 9.13d,f,h). From the time-domain CARS signal, the Raman spectrum can be simply calculated via Fourier transform (Figure 9.13e,g,i), similar to conventional interferometric Fourier transform CARS (FT-CARS) techniques [26,50]. Traditionally, the Fourier transform is computed from realizations taken at pulse separations greater than the pulse width to limit the non-resonant signal contribution.

### 9.3.3 Advanced Selective Excitation Techniques

#### 9.3.3.1 Alternative Shaping Functions for Enhanced Level Selectivity

Taking principles from FT-CARS and single-pulse experiments with periodic phase content, one can conduct full spectral analysis while suppressing or enhancing specific Raman lines. This concept was shown in a three-beam, femtosecond-pulse approach where the time delay between the first two (excitation) beams was scanned and was then subsequently probed [51]. In this configuration, it was shown that further mode selectivity can be achieved by adding periodic phase content in the excitation pulses to create satellite pulses. Specifically, this was done such that the periodic modulation matched the vibrational period. An enhancement was found for a particular Raman mode when the harmonic content and the delay between the two sets of pulses were
consistent with the vibrational period. Mode selectivity was attained throughout the scans of the delay between the two excitation pulses simply because even when the pulse separation matched the period of a specific level, the satellite harmonic pulses did not coherently contribute to the population. This technique has been shown to enhance the contribution from desired Raman levels while reducing the contribution from others as seen in the spectra computed by Fourier analysis (Figure 9.15a). The striking finding from this work is that the shaped pulses can lead to an increase in the energy and selectivity of a specific mode (compared to unshaped pulses) in the presence of a resonant electronic transition (Figure 9.15b).

A number of single-pulse, selective-excitation approaches have been developed based on the concept of applying cosine-based phase functions to alter the pathways leading to vibrational population. More recently, it has been demonstrated that selective excitation can be achieved using a variety of alternative periodic phase functions. One such variant to cosine modulation functions is the use of Pseudorandom Galois functions, which are strongly uncorrelated except at a specific frequency. A greater level of anti-correlation compared to cosine phase modulation among the off-resonant frequencies leads to higher selectivity of a particular desired frequency. This technique has been applied to various types of nonlinear optical applications, including two-photon excitation and stimulated Raman scattering [52]. It has also been shown that the use of periodic replica of random binary phases can be used to create constructive interference for a specific Raman mode [53]. Examples of binary Pseudorandom Galois functions applied to the excitation spectral phase are shown in Figure 9.16 where phase configurations can be tailored to populate specific levels.

9.3.3.2 Alternative Excitation Sources for Increased Detectable Raman Bandwidth

From Figure 9.16, it is clear how the pulse bandwidth hampers the ability to excite higher-energy Raman modes (energy different between pump and Stokes photons). When using single-pulse techniques, the upper and lower limits of CARS detection are
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restricted by the pulse bandwidth and proximity to the excitation pulse that CARS signal can be detected, respectively. Although techniques based on selective excitation can be implemented using a single detector, it has been shown that the use of a spectrometer can further aid in spectral filtering to effectively collect CARS signal closer to the excitation pulse bandwidth and hence resolve lower Raman lines. This has been demonstrated by von Vacano et al. where the excitation spectrum was cut near the central frequency to allow for higher energy at the lower end of the spectrum and thus enhance the signal of the lower lines (i.e., lowest detectable frequencies are probed by the bluest part of the spectrum) [54]. Using this technique, Raman modes below 200 cm\(^{-1}\) were readily resolved. Conversely, the upper limit of vibrational detection has been increased with the advent of ultra-broadband femtosecond sources. These octave spanning lasers have been employed in CARS measurements, allowing for detection of Raman lines higher than 4500 cm\(^{-1}\), as demonstrated with enhanced sensitivity afforded by spectral focusing [13]. It should be noted that the mentioned techniques for resolving a greater Raman bandwidth are also applicable to multiplexed techniques.

9.3.3.3 Heterodyne Amplification for Increased Sensitivity for Detection of Low Signals

One of the complications in conducting selective excitation experiments is that the CARS signals are typically very low. The low signal further increases measurement integration times and therefore limits the ability to use these techniques for imaging biological and other dynamic systems. One approach to enhance the inherently weak signals is to coherently use the excitation field as a local oscillator. Similar to multiplexed, phase-gated techniques, where CARS signals are amplified by the non-resonant background, it has been shown that part of the excitation field can effectively serve in a heterodyne

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**FIGURE 9.16** Selective excitation of Raman-active vibrational modes via binary phase shaping: (a) binary phase mask design for \(\Delta \Omega_p < 2 \Omega_R\); (b) binary phase mask design for \(\Delta \Omega_p \geq 2 \Omega_R\). (\(\Delta \Omega_p\) is the bandwidth of the pump Stokes part of the laser spectrum and \(\Omega_R\) is the transition Raman shift.) (Enhanced figure kindly provided by Marcos Dantus and colleagues, Wrzesinski, P.J. et al., *J. Raman Spectrosc.*, 42(3), 393, 2010. With permission.)
amplification scheme. The Motzkus group has shown that allowing a narrow, attenuated portion of the excitation spectrum to interact with the CARS signal results in a functional local oscillator that can amplify the CARS signal over three orders of magnitude [55]. The resulting heterodyne CARS intensity \( S(\omega) \) is linearly dependent on concentration and the phase function of the local oscillator (Equation 9.4). By choosing an appropriate phase function for the local oscillator, the heterodyne CARS signal can be optimized, thus increasing the sensitivity limit. Using such optimized local oscillator fields, Müller et al. successfully demonstrated sensitivity in the attomole regime corresponding to \( 5 \times 10^6 \) molecules in the focal volume [56].

\[
S(\omega) = I_{\text{CARS}}(\omega) + 2\sqrt{I_{\text{CARS}}(\omega)I_{\text{LO}}(\omega)} \times \cos[\Delta \phi(\omega)] + I_{\text{LO}}(\omega) \quad (9.4)
\]

\[
S^{(\text{HET})}(\omega) = 2\sqrt{I_{\text{CARS}}(\omega)I_{\text{LO}}(\omega)} \times \cos[\Delta \phi(\omega)]
\]

\( I_{\text{CARS}}(\omega) \propto |E_{\text{CARS}}(\omega)|^2 \) scales quadratically with the number \( N \) of scattering molecules. Mixing \( E_{\text{CARS}}(\omega) \) with the local oscillator field \( E_{\text{LO}}(\omega) \) in a square-law detector yields the signal \( S(\omega) \) where \( I_{\text{CARS}} \) and \( I_{\text{LO}} \) are the homodyne intensities of the CARS signal and the local oscillator, respectively. From this equation, \( S^{(\text{HET})} \) (the heterodyne interference term) scales linearly with \( N \) and thus the concentration of Raman scatterers. Maximum amplification is consequently achieved when \( \phi_{\text{LO}}(\omega) = \phi_{\text{CARS}}(\omega) + \Delta \phi(\omega) \) [55].

### 9.3.3.4 Two Color Single-Beam CARS with Independent Probe Shaping for Multi-Octave Frequency Resolution

A caveat in typical implementation of single-pulse CARS, via phase-only periodic modulations, is the limit of detection to one frequency octave. For the sake of simplicity, this complication arises due to the presence of multiple pulses in excitation train, which can excite a number of vibrational levels, namely, integer harmonics of all the possible frequencies generated by the multiple pulses, thus leading to ambiguity in which pulse serves as the probe. One solution to alleviate the single-octave restriction is to spectrally break a very broad pulse into distinct time-delayed pulses so that the probe is clearly separable from the pump and Stokes pulses in both the time and spectral frequency (Figure 9.17a). This can be done by applying a linear phase to a spectral band where the slope is directly related to the time delay as dictated by the Fourier relations. The result is two broadband pulses that are separated by a controlled time delay (Figure 9.17b). In this configuration, a transform-limited pulse provides the pump and Stokes photons to excite the molecular vibration while the second pulse acts as a probe. By scanning the delay between the pulses, the probe interacts with the molecule at various points during the oscillating polarization period and hence spectrally shifts the probe accordingly, that is, detected CARS signal. In contrast to conventional single-pulse CARS, the signal originating from the spectrally defined probe is exclusive detected. Specifically, the signal originating from probe photons in the first pulse is spectrally separated from the signal originating from probe photons in the second (spectrally different) pulse. The vibrational lines can then be resolved through analysis of the periodic, spectral oscillations of the detected CARS photons [57]. This approach can be further expanded upon in a technique that also incorporates selective excitation principles. For example, one can enhance the contribution from specific Raman line by applying a periodic
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modulation to the spectral region of the initial pulse, which provides the pump and Stokes photons (Figure 9.17c through f). As in the previously described selective excitation method, a specific mode is enhanced when the vibrational period matches that of the desired vibrational mode. This technique gains the benefits of selective excitation while eliminating the restriction of single-octave detection since the CARS signal originates from an exclusively defined probe, which is particularly beneficial when observing low wave numbers [58]. The theoretical and experimental considerations of the two-color approach have been studied extensively, particularly the effects of choosing the optimal spectral region to break the pulse and the benefits of also incorporating polarization-based detection for enhanced sensitivity due to removal of the non-resonant contribution [14].

9.3.3.5 Fast Pulse Shaping Techniques for Rapid Tunability of Excited Raman Levels

One of the ultimate goals of label-free techniques such as CARS is the application to biologically relevant problems. While a number of CARS studies have been performed on live specimens [2,59–62] and observed molecular dynamics [21], there is still a need for the development of tools to allow for faster scanning while using selective excitation techniques. It can be easily understood that rapid imaging can be achieved when interrogating

FIGURE 9.17 Generation of two-color double pulses from compressed supercontinuum. (a) Experimental spectrum with spectral phase \(\phi(\omega)\) (dotted line). (b) Simulated double pulse with corresponding delay \(\tau = 250\) fs. (Adapted from von Vacano, B. and Motzkus, M., Opt. Commun., 264, 488, 2006. With permission.) (c) Spectrum and spectral phase of the shaped excitation pulses, with the red part at lower frequencies acting as pump and Stokes, and the blue part as time-delayed probe. The spectral phase shown creates a temporal separation of the two spectra of 1300 fs, and an additional multi-pulse modulation on the pump/Stokes pulse with a temporal spacing of 420 fs. (d) A frequency-resolved cross correlation and (e) the integrated cross correlation measured in situ confirm the successful delivery of the desired pulse shape. (f) Measured CARS transients for the sample mixture (CHCl\(_3\) and CBrCl\(_3\)) with unshaped black curve and shaped gray curve pulses show direct control over the molecular oscillations. (Adapted from von Vacano, B. and Motzkus, M., J. Chem. Phys., 127, 144514, 2007. With permission.)
a single specific Raman level; however, it is often desired to simultaneously probe multiple Raman levels or interrogate an unknown sample and collect a full Raman spectrum. Particularly, a major challenge in both conventional multi-beam and single-beam selective-excitation techniques is the ability to rapidly tune the specific Raman mode under interrogation. In conventional multi-beam approaches, the speed of a spectral scan is therefore limited by the desired resolution, that is, number of spectral acquisitions, and dictated by the time required to detune the pump and Stokes beams (seconds). In single-beam selective excitation approaches, based on pulse shaping, the speed is also limited by the resolution, however dictated by the ability to change the spectral mask, which can be on the order of milliseconds when using a conventional SLM or as low as nanoseconds with more advanced devices such as acousto-optical modulators.

The ability to rapidly shape pulses has been previously studied using SLM techniques [63–67] and applied in CARS schemes [63,68]. One of the simplest adaptations to a traditional SLM-based, 4-f shaper is the ability to change phase shapes by scanning the spectrally spread beam in an additional dimension on a 2-D SLM, transverse to the spectral axis (Figure 9.18 inset). Using a 2-D SLM, Frumker et al. have shown that rapid shape selection is possible by imaging a galvanometric mirror on the grating of a 4-f shaper, prior to the Fourier lens, which thus enables one to scan the location of the beam on the SLM and addresses a series of phase patterns (Figure 9.18). This technique allows for independent phase patterns to be addressed once fixed on the SLM and changed at rates limited by the galvanometer. Using this technique, Frumker demonstrated pulse shaping up to 100kHz [66]. Such use of rapid phase scanning has demonstrated in a CARS and two-photon absorption schemes where the phase was alternated between shapes that maximize the constructive and destructive interference paths leading to

![Figure 9.18](image-url)
population of a vibrational [63,68] or electronic level [67], respectively. This technique readily allows for rapid acquisition with suppressed background using standard lock-in detection. Although this method has been used to rapidly observe a single Raman mode, full spectral information could be obtained by encoding the 2-D SLM with phases corresponding to a full range of temporally split pulses, and spectral information could be retrieved via real-time Fourier analysis with a spectrum analyzer.

Using a similar experimental configuration to Frumker et al., Levitt et al. demonstrated 80 kHz phase-only shaping for rapid selective-excitation measurements with multiplexed detection [68]. In this technique, a series of phase shapes are carefully chosen such that when scanned, the CARS signals from different chemicals are modulated at different frequencies (Figure 9.19a). This is achieved by first taking full time-domain scans of various pure chemicals and maximizing a cost function that identifies the necessary shapes (shapes corresponding to A–D) leading to the highest contrast between them upon rapid scanning, that is, lowest frequency correlation (Figure 9.19b). The various shapes are then updated on a 2-D SLM and scanned with a galvanometric mirror, resulting in the CARS signals modulated at different integer harmonics of the scan frequency, corresponding to the different chemical species (Figure 9.19c). The entire CARS signal is chemically discriminated using a dual-harmonic, lock-in amplifier and has been demonstrated with pixel dwell times of 500 μs in 3-D scans [68]. While this technique has proven capable to acquire multiplex measurements of two chemicals, it can be expanded to many more limited by the number of shapes that can be addressed on the SLM as the minimum number of shapes is two to the power of detectable chemicals.

![FIGURE 9.19](image.png) Schematic diagram for rapid multiplexed CARS detection. (a) The desired CARS intensity for sulfur and chloroform, modulated by a series sequentially scanned alternated phase shapes comprised of (b) four independent shapes (A–D). (c) When rapidly scanned, the CARS signal from sulfur and chloroform is modulated at the specified harmonic frequencies of the galvanometric mirror and detected via lock-in detection.
There have also been advances in improving acquisition speeds using techniques that reduce the number of required independent acquisitions. One such technique uses the concepts developed in the field of compressed sensing (or compressive sensing). In brief, it has been shown that an \( N \)-point signal can be reconstructed from much less than \( N \) Fourier measurements, under the assumption of sparse prevalence in the frequency domain [69,70]. This can be readily applied to the described selective-excitation CARS measurements as the number of vibrational spectra of simple molecules are usually sparse; therefore, the number of non-zero elements in the spectral domain is low and can be calculated from a similar number of temporal measurements. Using this technique, Katz et al. demonstrated a fourfold reduction in the number of temporal measurements necessary to accurately resolve sparse vibrational spectra (Figure 9.20) [71,72].

![Graphs showing time-domain and Fourier transform data](image)

**FIGURE 9.20** Experimental results of compressive-sensing Fourier transform vibrational spectroscopy using under-sampled time-domain data. (a) Raw time-domain trace for chloroform, containing 281 points (blue) and the randomly sampled 60 points (red). (b) Resolved vibrational spectrum from full data (blue), 60-point data using standard FT (green) and 60-point data using CS reconstruction (red). (Adapted from Wrzesinski, P.J. et al., *J. Raman Spectrosc.*, 42(3), 393, 2010.)

9.4 Future Outlook

While the concept of coherent control has been practiced for more than 20 years, the use of the technique for CARS has rapidly grown in the past decade. Throughout this time, the technical aspects of the implementations have been intensively studied and recently focused on applications. With further development of broadband sources, single-pulse CARS can be applicable to a greater range of applications afforded by the increased resolvable Raman bandwidth. Furthermore, development of techniques to preserve phase through scattering media can better allow shaped pulses to probe biologically...
interesting samples as done using conventional CARS methods. These advances in combination with fast shaping techniques can provide an attractive alternative to conventional multi-beam approaches. In the future, it would not be unlikely to see further development of single-beam techniques that employ pulse-shaping techniques due to the additional benefits afforded such as concurrent multi-modal detection of additional ultra-fast phenomena such as harmonic generation.

References

Chapter 9


**Author Query**

[AQ1] Please check all the heading levels identified in this chapter for correctness.