

Background-free broadband CARS spectroscopy from a 1-MHz ytterbium laser

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Abstract: We introduce a novel configuration for broadband, time-resolved CARS spectroscopy/microscopy in which pump, Stokes and probe pulses are all derived from a single femtosecond Yb:KYW laser. The 1-MHz repetition rate of the system allows very intense CARS signals to be obtained over short acquisition times, while a delayed probe pulse ensures an efficient non-resonant background suppression.

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1. Introduction

Coherent anti-Stokes Raman scattering (CARS) is a powerful technique for label-free, chemically sensitive identification of molecules [1,2]. It involves the excitation of a sample with two pulses at frequencies ω_{pu} (pump) and ω_{S} (Stokes), whose difference matches the frequency Ω of a Raman active molecular vibration. The interaction of a third pulse at frequency ω_{pr} (probe) with the vibrational coherence generated by pump and Stokes produces a strong coherent signal at the anti-Stokes frequency, $\omega_{\text{aS}} = \omega_{\text{pu}} - \omega_{\text{S}} + \omega_{\text{pr}}$. The probe pulse can be equal (two-colour CARS) or different (three-colour CARS) with respect to the pump. Single-frequency CARS allows a very high acquisition speed, but it gives only limited information on the molecular system under study. In many cases, the ability to distinguish between the different components within a complex heterogeneous system requires the recording of a full Raman spectrum. Broadband CARS [3,4] uses a narrowband probe pulse, providing spectral resolution, and a broadband Stokes pulse, enabling the detection of a complete vibrational spectrum.

A drawback of CARS, both in its single-frequency and broadband versions, is the presence of a non-resonant background (NRB), that does not carry any chemically specific information. The NRB is generated by the instantaneous electronic $\chi^{(3)}$ of the molecular species under study and of the surrounding medium, according to a four-wave mixing scheme $\omega_{\text{pu}} + \omega_{\text{pr}} = \omega_{\text{S}} + \omega_{\text{aS}}$, with the annihilation of two photons at ω_{pu} and ω_{pr} and the simultaneous creation of two photons at ω_{S} and ω_{aS} . When the concentrations of the target molecules are low, such NRB can distort and even overwhelm the resonant signal of interest. Several methods for NRB suppression have been proposed, such as polarization-sensitive CARS [5], frequency-modulation CARS [6], interferometric CARS [7] or, for the case of broadband CARS, retrieval of the resonant contribution through proper spectral manipulation [8,9]. Alternatively, the NRB can be avoided using stimulated Raman scattering (SRS), which detects the stimulated emission induced by the Stokes pulse from a virtual state, excited by the pump pulse, to the probed vibrational state [10]. Broadband SRS could in principle provide a vibrational spectrum free from NRB, analogous to the one obtained with spontaneous Raman [11]. However it presents the technological challenge of being able to detect small changes in the Stokes/pump signals, of the order of 10^{-4} or less, over broad bandwidths. In fact high modulation speed lock-in schemes, which are commonly employed for single-frequency SRS, cannot be easily extended to broadband detection.

A particularly powerful and elegant approach for NRB suppression is time-resolved CARS (TR-CARS) [12,13], in which the probe pulse is delayed with respect to the pump/Stokes pair by a time Δt which is sufficiently high to avoid any temporal overlap. In such case the NRB generated by the $\omega_{\text{pu}} + \omega_{\text{pr}} = \omega_{\text{S}} + \omega_{\text{aS}}$ process, which relies on the instantaneous $\chi^{(3)}$ of the medium, is completely suppressed. The price to be paid is that the time-delayed probe pulse interacts with a vibrational coherence that has decayed with dephasing time T_{2v} , leading to a reduction of the useful CARS signal by $\exp(-2\Delta t/T_{2v})$. TR-CARS requires a three-colour configuration, to prevent spectral overlap with the NRB generated by the $2\omega_{\text{pu}} = \omega_{\text{S}} + \omega_{\text{aS}}$ process. The generation of three independent synchronized pulses makes TR-CARS quite complicated; for this reason, the technique has been initially implemented using amplified Ti:sapphire laser systems [14], providing enough pulse energy

to generate multiple colours through optical parametric amplification. An alternative TR-CARS scheme has been recently demonstrated starting from a simpler two-colour configuration, where the frequency components of an ultrashort continuum pulse provide simultaneous pump/Stokes colours, and a time-delayed narrowband probe generates the NRB-free CARS signal [15–17].

So far, the laser sources used for TR-CARS have been either oscillators, with high repetition rate (≈ 100 MHz) and low pulse energy (a few nJs) or amplified Ti:sapphire systems, with low repetition rate (≈ 1 kHz) and high pulse energy (a few mJs). The recent development of all-solid state femtosecond Yb-based systems, either in the bulk or in the fiber format, has allowed accessing an intermediate parameter range, with repetition rate up to ≈ 1 MHz and energy of several μ Js. This regime has not yet been deeply explored for nonlinear spectroscopy/microscopy, but it offers an interesting compromise between high pulse energy, enhancing the non-linear effects, and high repetition rate, enabling fast acquisition times. Besides, diode pumping makes these sources particularly compact and reliable, and thus amenable to in-field operation. In this work we present a simple setup for broadband TR-CARS spectroscopy based on a single femtosecond Yb:KYW laser. The system allows generating the three synchronized colours - pump, broadband Stokes and narrowband probe - in a straightforward fashion, enabling the acquisition of broadband, NRB-free CARS spectra with very high signal-to-noise ratios and short acquisition times.

2. Experimental setup

The experimental setup used for the 3-colour broadband TR-CARS is sketched in Fig. 1. It starts with a regeneratively amplified Yb:KYW laser (femtoREGEN, HighQLaser) based on a dual-head cavity and producing 1040-nm, 350-fs pulses (60 cm^{-1} bandwidth) with an average power up to 8 W and a repetition of 1 MHz. The laser output is split into three beams, used to generate the three required colours: pump, broadband Stokes and narrowband probe. The pump is produced by second-harmonic generation in a 8-mm-long lithium triborate crystal, resulting in 520-nm pulses with $\approx 60\text{ cm}^{-1}$ bandwidth (500-fs duration). The Stokes is obtained by white-light continuum (WLC) generation in a bulk medium, focusing a $\approx 4 \div 5\ \mu$ J fraction of the available energy in a 4-mm-thick YAG plate (it has been shown [18] that low-

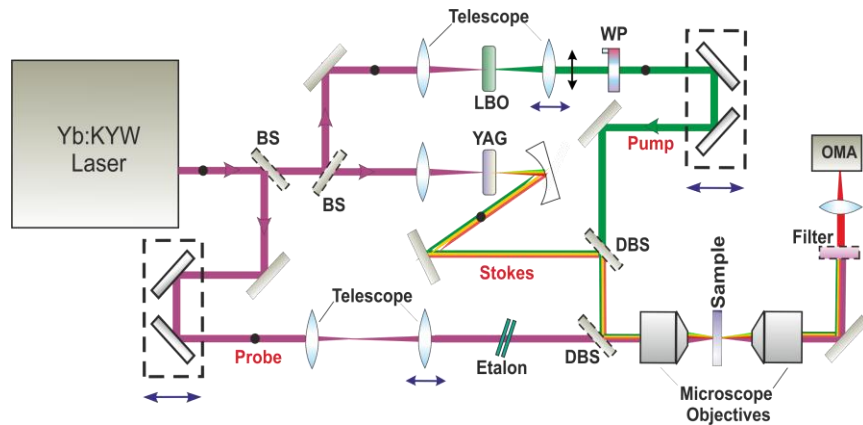


Fig. 1. Schematic diagram of the experimental setup for three-colour TR-CARS. BS: beam splitter; DBS: dichroic beam splitter; LBO: lithium triborate; WP: half-wave plate; OMA: optical multichannel analyzer.

bandgap materials such as YAG enable the generation of a stable and spectrally flat WLC even with relatively long pulses, such as the ones used here). The blue portion of the WLC from 500 to 630 nm is selected by a short-pass filter, to avoid spectral superposition with the three-colour CARS signal: it is spectrally quite flat and displays a remarkable shot-to-shot stability, with rms fluctuation lower than 1%. In combination with the Raman pump at 520

nm, it enables the simultaneous excitation of all vibrational modes of interest, from low frequencies up to $\approx 3300 \text{ cm}^{-1}$. After spectral filtering the average power of the Stokes beam amounts to nearly 1 mW. The third beam is finally used to produce a narrowband probe at 1040 nm. Spectral narrowing is passively achieved by means of a properly designed etalon (SLS Optics Ltd.) providing a finesse of 12 and a free-spectral-range of 85 cm^{-1} , which results in an overall nominal spectral resolution of 7.5 cm^{-1} . Figure 2 reports in a normalized scale the spectra of pump, Stokes, and probe beams. The experimental probe spectrum is better resolved in the inset: it exhibits the expected Lorentzian shape, with a FWHM of 13 cm^{-1} (9 cm^{-1} after deconvolution with the spectrometer response) without any side lobe given by adjacent resonances of the etalon. It is worth noting that the Lorentzian transmission spectrum of the etalon, which corresponds to a pulse temporal profile consisting of a sharp rise followed by an exponential decay [19], is very much suited to the purpose of an efficient TR-CARS interaction. On one hand the sharp rise allows for an efficient suppression of the NRB since it gives minimum temporal overlap with the pump and Stokes pulses; on the other hand the exponential decay can be chosen to match the typical dephasing time of the vibrational coherence, thus maximizing the interaction with the sample. The three-colour CARS falls in the spectral region between 1040 nm (corresponding to zero frequency detuning) and 775 nm (3300 cm^{-1}), and can thus be efficiently detected by a silicon spectrometer.

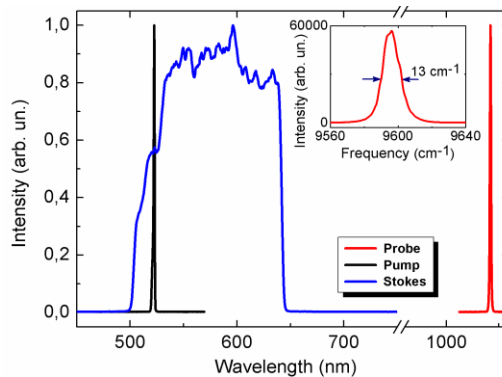


Fig. 2. (a): spectra of the pump (black), Stokes (blue) and probe (red) pulses. (b): zoom of the probe spectrum indicating a 13 cm^{-1} FWHM (9 cm^{-1} after deconvolution with the spectrometer response).

Pump, Stokes and probe pulses are collinearly superimposed with dichroic beam splitters and focused on the sample by a 0.7 NA microscope objective. Telescopes on the pump and probe arms are adjusted to match the focal planes of the three beams. A computer-controlled delay line ensures reproducible delay of the probe pulse with respect to the pump/Stokes pair. The CARS signal, selected by a suitable combination of long- and short-pass filters, is sent to a commercial optical-multi-channel-analyzer (OMA, Princeton Instruments SP2150) with $\approx 4 \text{ cm}^{-1}$ spectral resolution and a maximum acquisition speed of 1 kHz.

It is interesting to compare the performance of our 1-MHz system with those of standard broadband CARS systems based on femtosecond Ti:sapphire oscillators [3,15–17,20]. We start by recalling that the instantaneous CARS intensity is proportional to the product of the intensities of the three interacting beams, according to the formula $I_{CARS} \propto I_{pu} I_S I_{pr}$. By relating the intensities to the corresponding average power levels P and to the laser repetition-frequency f_{rep} through the approximated relationships $I = U/\tau A$ and $P = U f_{rep}$ - where U , τ and A are the pulse energy, the pulse-width and an effective area for the beam cross-section, respectively - one readily finds $P_{CARS} \propto P_{pu} P_S P_{pr} / (\tau A f_{rep})^2$, where the same τ and A have been considered, for the sake of simplicity, for all beams. One can thus see that the CARS power scales as $1/(f_{rep})^2$, with the consequence that for comparable average-power values of the three

beams, moving from an oscillator ($f_{rep} = 50 \div 100$ MHz) to an Yb-based amplifier ($f_{rep} \approx 1$ MHz) increases the CARS signal by 3 to 4 orders of magnitude.

3. Results and discussion

To assess the potential of our system for broadband CARS spectroscopy, we performed preliminary experiments with a simplified two-colour configuration, using the 520-nm pump and the WLC Stokes. Although the Stokes pulse is broadband enough to enable covering of all vibrational frequencies from 0 to 3300 cm^{-1} , the dispersion introduced by the refractive optics on its path (in particular the microscope objective) must be carefully compensated to ensure temporal overlap of all its colours with the relatively short (≈ 300 fs) pump pulse. While this can be done using suitable dispersive delay-lines (prism compressor or chirped mirrors) for these experiments we concentrated on the $2400\text{--}3200\text{ cm}^{-1}$ spectral region, covering the CH bonds, which is of interest for many applications. Figure 3(a) reports the 2-colour broadband CARS spectra of several solvents. Due to the high peak intensities provided by our system, the two-colour CARS signal (which falls in the 445–460 nm wavelength range) was very intense, amounting to ≈ 200 nW for methanol when using a 10 mW level of pump/probe power. This signal heavily saturates our OMA even for the shortest acquisition times (1 ms), thus in principle enabling acquisition of spectra at much higher speeds. Even if qualitatively in agreement with the corresponding Raman spectra, these two-colour CARS spectra are affected by two main problems: a rather poor frequency resolution, which results from the $\approx 60\text{ cm}^{-1}$ spectral width of the pump beam, and the asymmetrical dispersive shape of the main peaks, which is due to the coherent superposition with a strong NRB.

Figure 3(b) shows three-colours CARS spectra of methanol, for different delays between the probe pulse and the pump/Stokes pair. The typical signal levels of these spectra range from 1 to 3 nW average power. At time zero, the spectrum still displays the characteristic dispersive shape due to interference with the NRB and closely resembles the two-colour CARS, although with higher spectral resolution due to the narrower width of the probe. Due to the peculiar truncated exponential profile of the probe pulse, a delay of $\Delta t = 330$ fs is already sufficient to completely suppress the NRB, making the shapes of the two main resonances much more symmetrical and shifting their maxima to the 2830 and 2945 cm^{-1} values that are expected from the spontaneous Raman spectra of the molecule.

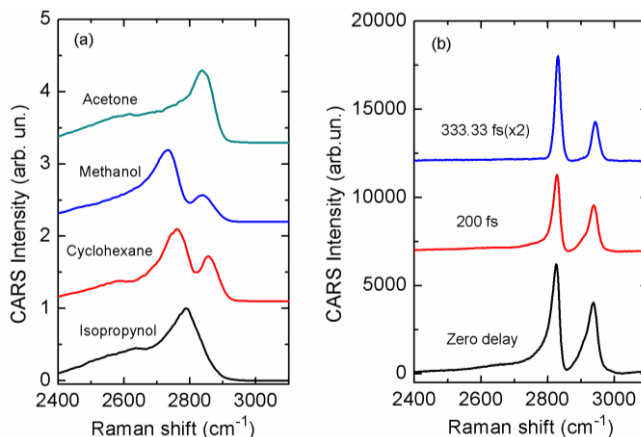


Fig. 3. (a) Two-colour CARS spectra of different solvents; (b) three-colour TR-CARS spectra of methanol as a function of the delay of the probe pulse with respect to the pump/Stokes pair.

Figure 4(a) reports three-colour CARS spectra of various solvents. Even the rather congested spectrum of isopropynol is now perfectly resolved. Due to imperfect mode-matching between the three beams, the overall CARS signal is reduced with respect to the two-colour case, but it is still sufficient to nearly saturate the OMA with 1-ms acquisition

time. Given the very high signal-to-noise of the spectra, it is reasonable to foresee that a dedicated and faster spectrometer could acquire CARS spectra within significantly shorter times, enabling high-speed, background-free, broadband vibrational imaging.

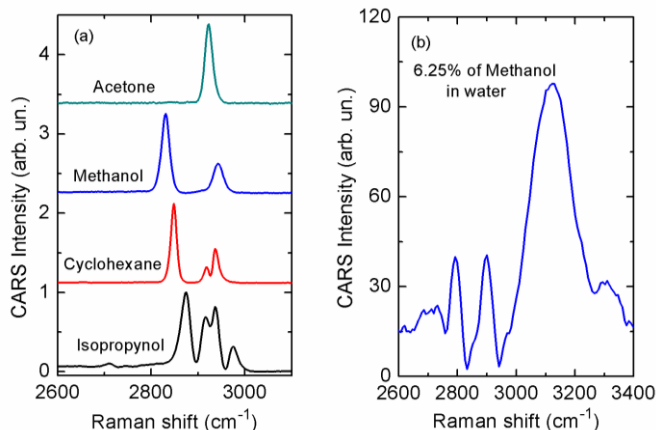


Fig. 4. (a) Three-colour TR-CARS spectra of different solvents at $\Delta t = 330$ fs; (b) TR-CARS spectrum of a 6.25% diluted solution of methanol in water.

To assess the sensitivity of our system, we studied solutions of methanol diluted in water. Figure 4(b) reports a TR-CARS spectrum for a 6.25% methanol concentration. Even at such a strong dilution factor, the spectral features of methanol are clearly resolved with respect to the huge water resonance. By software analysis the water response could even be subtracted, allowing for full chemical identification of the sample even at significantly higher dilutions. This example shows how the broadband capability can be successful in the identification of molecular compounds with more or less congested spectral features even within environments giving strong non-resonant and also resonant contribution.

4. Conclusion

In this work we have presented a setup for broadband three-colour TR-CARS spectroscopy based on a single femtosecond Yb:KYW laser system. Pump, broadband Stokes and narrowband probe are generated in a straightforward fashion by direct non-linear and linear manipulation of the Yb:KYW pulses. Shaping of the probe pulse by an etalon gives the optimum temporal profile for efficient NRB suppression. The combination of high repetition rate (1 MHz) and pulse energy (μJ -level) guarantees intense CARS signals, enabling short acquisition times for the spectra.

The rapid technological development of Yb-based femtosecond lasers, which become increasingly powerful, compact and reliable, makes our solution of interest for high-speed vibrational spectroscopy/imaging. The use of a pump pulse in the visible (520 nm) implies a limited applicability of the system to the imaging of biological compounds, due to the damage induced by two-photon absorption. On the other hand, in other applications such as pharmaceuticals [21] and micro-fluidics [22], for which photodamage is of a lesser concern, it could become a work-horse for vibrational detection and identification of molecules.

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