Coherent Raman spectroscopy with a fiber-format femtosecond oscillator[†]

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We report on the recent development of a new technological approach for coherent Raman spectroscopy/microscopy based on spectral compression of femtosecond pulses emitted by an amplified multiple-branch Er:fiber oscillator. Spectral compression is achieved by group-velocity mismatched second-harmonic generation in periodically poled nonlinear crystals, and it allows efficient synthesis of multiple synchronized narrow-bandwidth picosecond pulses with frequency difference continuously tunable from 1000 to 3500 cm⁻¹. The system offers performances close to the current state of the art both for coherent anti-Stokes Raman scattering (CARS) and for stimulated Raman scattering (SRS), but with significant advantages in terms of compactness and versatility. In fact, several configurations can be easily implemented, including multiplex CARS, two-color imaging and nonresonant background suppression in CARS. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

Optical microscopy has the unique capability of imaging biological samples with resolution down to the few hundred nanometer range. Despite its very high sensitivity, down to the single-molecule limit, fluorescence microscopy requires sample staining with fluorescent marker molecules. Such labels often have sizes comparable with the molecules under study, thus altering the biological functionality. Raman scattering microscopy overcomes this limitation by providing an intrinsic contrast mechanism, based on the characteristic vibrational frequencies of the investigated molecule, allowing for noninvasive, label-free imaging of tissues and cells. Although spontaneous Raman scattering yields weak signals and thus limited imaging speeds, the sensitivity can be boosted by many orders of magnitude by the use of coherent Raman scattering (CRS).^[1]

Until recently, the most popular form of CRS has been coherent anti-Stokes Raman scattering (CARS).^[2] In CARS, two synchronized narrowband pulses, the pump (frequency ω_p) and Stokes (frequency ω_s), are focused on the sample, and their difference frequency is tuned to a Raman-active molecular vibration $\Omega = \omega_p - \omega_s$. When this occurs, a strong anti-Stokes signal is generated at $\omega_{as} = 2\omega_p - \omega_s$, providing a chemically specific signature that can be used to uniquely identify the molecule. CARS has the advantage of being a virtually background-free process, because the emitted signal has a frequency differing from those of pump and Stokes, allowing very high acquisition speeds, up to the video rate.^[3] On the other hand, the CARS signal is given by

$I_{\text{CARS}} \propto |\chi^{(3)}|^2 = |\chi_R^{(3)}(\Omega) + \chi_{\text{NR}}^{(3)}|^2$, where $\chi_R^{(3)}(\Omega)$ is the complex resonant response and $\chi_{\text{NR}}^{(3)}$ is the real nonresonant background (NRB), which does not carry any chemically specific information. Because $\chi^{(3)}$ is proportional to the density of oscillators N , the CARS signal scales as N^2 , so that it fails to detect molecules at low concentrations. In addition, CARS is plagued by the presence of NRB, which is generated both by the molecular species under study and by the surrounding medium according to a four-wave

mixing scheme, with the absorption of two photons at ω_p and the simultaneous emission of one photon at ω_s and one photon at ω_{as} . When the concentrations of the target molecules are low, such NRB can distort and even overwhelm the resonant signal of interest. Several techniques have been proposed for NRB suppression. Frequency-modulation CARS (FM-CARS) requires the generation of a second Stokes (pump) field at a slightly different frequency so as to modulate the difference $\omega_p - \omega_s$ in and out of the vibrational resonance.^[4,5] The NRB, which is independent of frequency detuning, does not contribute to the detected modulated signal and therefore is efficiently suppressed. Alternatively, interferometric CARS (I-CARS) requires the generation of an intense field [local oscillator (LO)] at the anti-Stokes frequency, phase-coherent with the pump and Stokes fields, which interferes with the CARS field.^[6–9] By properly adjusting the phase of the LO with respect to the CARS signal, one can suppress the NRB and at the same time amplify the CARS signal. Both FM-CARS and I-CARS are, however, not easy to be implemented as they require the generation of a third narrowband pulse synchronized with pump and Stokes.

Both N^2 scaling and NRB limitations of CARS can be overcome by the stimulated Raman scattering (SRS) technique.^[10,11] In SRS, when the frequency difference between pump and Stokes pulses matches a vibrational mode, amplification of the Stokes pulse (and simultaneous depletion of the pump) occurs via stimulated emission from a virtual state to the probed vibrational state.^[12]

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Experimentally, either stimulated Raman gain (SRG) of the Stokes or stimulated Raman loss (SRL) of the pump can be measured. The SRS signal is proportional to the imaginary part of the third-order nonlinear susceptibility: $\Delta I_{\text{SRS}} \propto \text{Im}(\chi^{(3)}) = \text{Im}(\chi_R^{(3)}(\Omega))$. Therefore, SRS is inherently free from NRB, which is related to the real part of $\chi^{(3)}$, and in addition, it scales as N , thus allowing weakly concentrated species to be revealed; on the other hand, because it is based on the detection of a weak differential transmission signal (SRG or SRL), it requires the use of sophisticated low-noise acquisition techniques. Such high level of sensitivity is particularly challenging to be obtained at high acquisition speeds,^[13] leaving CARS as the technique of choice for several applications.

Despite the considerable potential of CRS techniques for life sciences,^[14] their widespread practical application has been so far limited by the complexity of the laser systems used for generating pump and Stokes beams. In fact, Raman transitions exhibit in the condensed phase typical linewidths of the order of few tens of cm^{-1} , which implies the need for narrowband, tunable pump and Stokes pulses, with picosecond duration, in order to efficiently excite the system while preserving molecular selectivity. In addition, high pulse repetition rates (tens of MHz), to maximize acquisition speed, and near-infrared (700–1000 nm) excitation wavelengths, to increase tissue penetration and minimize photodamage, are required. Initial CRS experiments were based on 2-ps Ti:sapphire lasers tightly synchronized by a suitable electronic active control,^[15] resulting in a very complex, bulky and costly setup. A more recent configuration, which represents the current state of the art in coherent Raman imaging, is based on an optical parametric oscillator (OPO) pumped by a picosecond Nd:YVO₄ oscillator.^[16] Such approach does not solve, however, the problem of cavity synchronization, which is required between OPO and pump laser; furthermore, it has limited flexibility, because it does not easily allow the generation of a third, independently tunable beam, as would be required for NRB suppression schemes or for two-color probing architectures.

The generation of tunable synchronized picosecond pulses is technically a nontrivial task. On the other hand, femtosecond sources are becoming more and more compact and reliable and allow for easy tunability over broad spectral ranges thanks to the nonlinear effects that can be driven by such high peak power short pulses. For this reason, several techniques have been proposed for the synthesis of tunable narrowband picosecond pulses starting from femtosecond pulses.^[17,18] We have recently demonstrated a simple yet powerful method for the generation of tunable narrowband picosecond pulses by spectral compression of femtosecond pulses through a second-harmonic generation (SHG) process. Indeed, when strong group-velocity mismatch occurs between fundamental frequency (FF) and second harmonic (SH) in a given interaction, the SH can exhibit picosecond duration with nearly transform-limited time–bandwidth product (spectral width below 10 cm^{-1}), the duration being essentially determined by the difference between FF and SH group delays.^[19,20] The SHG processes in the aforementioned conditions can easily achieve conversion efficiencies up to 40%.

In this paper, we describe in detail a CRS system with a setup radically simplified over existing solutions, by combination of the spectral compression technique with a compact femtosecond fiber laser. This system was recently demonstrated in both the CARS^[21,22] and the SRS^[23] configurations, and we present here the first results on an upgraded version with considerably higher peak power levels. Besides the advantages of compactness and cost, this system offers the added flexibility of a fiber-format oscillator with several amplified branches, which make it possible to generate a third beam to be employed either for the simultaneous

detection of multiple molecular species or for the implementation of NRB suppression techniques in CARS. Provided microscope objectives with near-infrared antireflection-coating are used, the available power levels, i.e. $\sim 100 \text{ mW}$ for the pump and $\sim 10 \text{ mW}$ for the Stokes at 40-MHz repetition frequency, allow for state-of-the-art performances in both the CARS and the SRS configuration. Optionally, by exploiting the inherently broad bandwidth of the laser pulses and supercontinuum generation processes in a highly nonlinear fiber (HNLF), broadband Stokes pulses can be synthesized, giving access to a multiplex CRS regime in which a wealth of molecular signatures can be addressed at once.

Spectral Compression Technique: Rationale

The fiber laser system used in the experiments easily generates widely tunable femtosecond pulses; however, for the single-color CARS/SRS applications, narrowband pulses are required. Several linear and nonlinear techniques have been proposed for the synthesis of tunable picosecond pulses starting from femtosecond pulses. Linear approaches, relying on spectral filtering of the femtosecond pulse with either a band-pass filter^[24] or the combination of a slit with a 4f pulse shaper,^[25] introduce a strong power penalty by an amount equal at least to the ratio between input and filtered bandwidth. Higher efficiency can be obtained with nonlinear methods. Self-phase-modulation processes in photonic crystal fibers with negatively chirped input pulses allow for compression ratios as high as 10, at the price, however, of poor power scalability and stability.^[17] Second-order nonlinear processes driven by chirped pulses have also been exploited, such as sum-frequency generation (SFG) between pulses with opposite chirp^[18] or difference-frequency generation between pulses with the same chirp.^[26] These techniques are, however, experimentally challenging, because they require the use of a pair of carefully balanced gratings (or prisms) pulse stretchers/compressors.

Recent papers^[19,20,27] showed that an SHG process in the presence of high group-velocity mismatch between the FF and the SH pulse can lead to the efficient generation of narrowband SH pulses starting from broadband FF ones. This result can be understood by considering that, in addition to the SHG process, there is also an efficient SFG process between spectral components of the FF that are symmetric with respect to the SHG phase-matching frequency, allowing efficient energy transfer from the broadband FF pulse to the narrowband SH one. To discuss the choice of the spectral compression crystal, it is worth remembering that the full width at half maximum bandwidth of the SH pulse $\Delta\nu_{\text{SH}}$ is approximately given by $\Delta\nu_{\text{SH}} = 0.886(1/|\delta|L)$,^[28] where L is the crystal length and $\delta = (1/v_{\text{gFF}}) - (1/v_{\text{gSH}})$ is the temporal walk-off per unit length, with v_{gFF} and v_{gSH} being the group velocities at the two frequencies. To achieve large compression ratios, one thus requires long crystals and large values of $|\delta|$. Periodically poled crystals are the best choice because of the following advantages^[29]: (1) high nonlinear coefficient, allowing efficient conversion even with relatively low peak powers; (2) high δ values, due to the large material dispersion and because, in quasi phase matching, the FF and SH are made to interact with the same polarization (parallel to the crystal optical axis); (3) absence of spatial walk-off, which allows for the use of relatively long crystals, leading to large compression ratios, combined with tight focusing.

Figure 1. Architecture of the adopted laser system, driven by an Er: fiber oscillator. BS, beam splitter; EDFA, Er-doped fiber amplifier; HNLF, highly nonlinear fiber; PPLN: periodically poled lithium niobate.

Experimental Setup

The architecture of the femtosecond laser system (FemtoFiber pro, from Toptica Photonics) driving our CARS/SRS setup is shown in Fig. 1. It starts with a mode-locked Er: fiber oscillator, with linear cavity and semiconductor saturable absorber mirror, working at 40-MHz repetition rate. The oscillator output is used to feed three independent Er-doped fiber amplifiers (EDFAs), each producing 350-mW average power, corresponding to ~ 9 nJ per pulse, at a 1560-nm central wavelength. All three EDFA outputs, which are synchronized and phase coherent, are compressed to nearly transform-limited sub-100-fs duration by a silicon prism pair.^[30] Two of the EDFA outputs are coupled to an HNLF for spectral broadening. The HNLF (3.7- μ m core diameter, ~ 7 -cm length) has a zero dispersion wavelength, which is close to, but slightly shorter than, the input laser wavelength. The pulses propagating in the anomalous dispersion regime undergo considerable spectral broadening, with the spectral energy density concentrating in two peaks on opposite sides of the input wavelength. At longer wavelengths, the pulse gives rise to a soliton, which experiences self-frequency shift due to intrapulse Raman scattering.^[31] The soliton is accompanied by a phase-matched dispersive wave at shorter wavelengths, propagating in the normal dispersion regime. The exact positions of the peaks of soliton and dispersive wave sensitively depend on the overall dispersion of the input pulse, which can be controlled by acting on the silicon prism pair insertion.^[32] It is thus possible to continuously tune the soliton peak between 1700 and 2100 nm (Fig. 2

(a)) and to push the dispersive wave to wavelengths as short as 1000 nm.^[33]

The system makes use of two distinct MgO-doped periodically poled lithium niobate (PPLN) crystals to generate the pump and Stokes pulses according to the spectral compression technique described earlier. The 1560-nm output of the EDFA is compressed by a 10-mm-long PPLN with a poling period of 19.3 μ m and generates the pump pulses at a fixed wavelength of 780 nm, with a 120-mW average power and a 15 cm^{-1} linewidth (see spectrum on the left of Fig. 2(b)). The redshifted soliton is frequency doubled with a 10-mm-long PPLN crystal having a fan-out grating spanning the range of 22–33 μ m, and it produces Stokes pulses tunable from 840 to 1100 nm with power up to 10 mW, as shown in Fig. 2(b). In this way, it is possible to cover with the Stokes pulse a wide range ($1000\text{--}3500\text{ cm}^{-1}$) of biologically relevant frequencies. Rapid tuning of the Stokes is achieved by transversely translating the fan-out crystal. Translation is currently performed manually, but the use of a motorized stage could give automatic wavelength selection and reproducibility. The linewidth of the generated Stokes pulses ranges between 18 and 30 cm^{-1} , which is somewhat higher than the data reported in the works by Marangoni *et al.*^[21] and Gambetta *et al.*^[23] This is due to the use of a shorter crystal and to a slight frequency smearing effect induced by the fan-out pattern.

The setup used for CARS and SRS experiments is reported in Fig. 3. Pump and Stokes pulses are synchronized by a delay line, collinearly combined by a dichroic beam splitter (LP02-785RS-25, from Semrock) and focused by a microscope objective [Nikon 60 $\times$, numerical aperture (NA)=0.80, working distance (WD)=3 mm]; the transmitted light is collimated by a long WD objective (Zeiss 100 $\times$, NA=0.75, WD=3 mm). For CARS detection, a notch filter (Thorlabs NF785/33) and a band-pass filter (custom-made from CVI) select the forward signal, with an overall rejection of 10^{13} on the pump and Stokes beams. For SRS detection, the Stokes pulse, filtered from the pump by a sequence of notch filter (Fig. 3) and a long-pass filter (Semrock 834/LP), is sent to a balanced InGaAs photodiode (New Focus Nirvana 2017). A fraction of the Stokes beam is split off before the beam splitter and is focused on the detector to serve as a reference. The pump beam is modulated acousto-optically at a 70-kHz frequency (APE GmbH AOM-80-D), and a lock-in amplifier (Stanford Research System SR830DSP) measures the SRG of the Stokes. Balanced detection largely cancels probe fluctuations and allows one to achieve a sensitivity down to $5 \cdot 10^{-7}$.

Figure 2. (a) Spectrum of the main laser output at 1560 nm (black line) and examples of spectra of the long-wavelength part of the supercontinuum (blue, cyan and red), tunable by acting on the input pulse chirp. (b) Spectra of the pump (green line) and of the tunable Stokes pulse (red lines), as obtained by spectral compression of the spectra reported in (a). This figure is available in colour online at wileyonlinelibrary.com/journal/jrs.

Figure 3. Scheme of the experimental apparatus used for coherent anti-Stokes Raman scattering and stimulated Raman scattering. AOM, acousto-optic modulator; BS, beam splitter; DBS, dichroic beam splitter; PD, photodetector; VA, variable attenuator.

Results and Discussion

The spectra of several solvents were acquired in order to test the performances of the system and to compare them with those obtained with a previous dual-branch fiber system,^[21,23] operating at 100 MHz with power levels lower by a factor of ~ 3 for the pump (40 mW) and up to 5 for the Stokes (1 mW at 1000 nm). Figure 4(a,b) shows the spectra in both the CARS and the SRS regimes when varying the frequency detuning between pump and Stokes by translation of the fan-out PPLN crystal. As expected, the CARS signatures are narrower because of the quadratic dependence on the nonlinear susceptibility, and they are also asymmetrically shaped because of the NRB contribution. The spectral resolution is currently limited to $\sim 40 \text{ cm}^{-1}$, but it could be improved with a better design of the fan-out crystal. On the other hand, the new setup allowed for much higher CARS and SRS signals, because of the combination of a lower repetition rate, higher power level and slightly shorter pulses, resulting in higher peak power. Simple calculations show, in fact, that, given the same interaction geometry and sample, the CARS average optical power scales proportionally to $P_p^2 P_s / f_{\text{rep}}^2$, whereas the SRG signal scales proportionally to P_p / f_{rep} , with P_p and P_s being the average power of pump and Stokes, respectively, and f_{rep} the laser repetition rate.^[34] The expected signal enhancement is, thus, as high as 500 for CARS and ~ 10 for SRS, which are values confirmed in the experiments: for methanol, e.g. the CARS average power was in excess of 400 pW and the SRG of the order of 10^{-3} . Concerning SRS, it is worth noting that the advantage given by

the signal enhancement was somehow traded off by a higher level of noise, limiting the sensitivity to $\sim 5 \cdot 10^{-7}$ over 500-ms integration time ($2 \cdot 10^{-7}$ with the previous system): this was due to increased intensity fluctuations in the supercontinuum, which were not perfectly canceled by the balanced detection system.

Figure 5 shows the results of a dilution test of acetone in water down to a 0.1% volume concentration value, in both the CARS and the SRS configurations. As expected, the CARS signal decreases quadratically, but it quite quickly reaches a constant value because of the strong NRB contribution given from water, limiting the sensitivity to $\sim 10\%$ volume concentration. Differently, as evidenced in the inset, the linear SRS response allows the detection of lower concentrations, down to $\sim 0.5\%$, as limited by the undesired resonant response of water, which extends down to the 2910 cm^{-1} pump–Stokes detuning adopted in the experiments.

Besides higher average power and energy levels, the new system presents another advantage with respect to the previously adopted dual-branch system at 100 MHz, which is the presence of a third amplified arm whose architecture and performance essentially replicate those of the second arm. The only difference concerns the possibility of easily reconfiguring its output as a broadband Stokes beam spanning the range of 950–1050 nm, or as a second narrow-band Stokes beam with tunability from 840 to 1100 nm (Fig. 1), or as a phase-coherent beam at the anti-Stokes frequency for I-CARS. Such arm adds considerable flexibility to the system as it provides an additional pulse, synchronized with the first two, which can be employed to implement different CRS configurations. In the most straightforward setup, the third arm is used to generate by spectral compression a second, independently tunable Stokes pulse, which can be applied to two-color CARS/SRS microscopy. This is shown in Fig. 6(a), in which the second arm generates a Stokes pulse at $\sim 890 \text{ nm}$, whereas the third arm, equipped with a PPLN crystal, generates a second Stokes pulse at $\sim 1020 \text{ nm}$. With this setup, it becomes possible to have simultaneous imaging in the fingerprint and the CH stretching regions in a much simpler fashion with respect to previous attempts using a pair of synchronized OPOs.^[10]

The third arm also enables the straightforward implementation of NRB suppression approaches, such as FM-CARS and I-CARS. For FM-CARS, the third arm can be used to generate a second, slightly detuned (by $\sim 100 \text{ cm}^{-1}$) Stokes pulse (Fig. 6(b)), which is alternated with the on-resonance Stokes pulse. For I-CARS, the third arm can be employed to generate an LO pulse at the anti-Stokes frequency (Fig. 6(c)) by SHG of the blueshifted dispersive wave.^[21] The phase coherence between LO and CARS signal is ensured by the fact that pump, Stokes and LO pulses are all derived from the same laser oscillator.

Figure 4. (a) Coherent anti-Stokes Raman scattering (CARS) and (b) stimulated Raman scattering (SRS) spectra of different solvents.

Figure 5. Dilution curves of acetone in water measured with coherent anti-Stokes Raman scattering (CARS) (circles) and stimulated Raman scattering (SRS) (diamonds) when tuned to the peak of the aliphatic CH stretching vibration, together with quadratic and linear fitting curves, respectively. Inset shows a zoom for low acetone concentration. Pump power was ~50 mW, and Stokes power was ~5 mW. SRG, stimulated Raman gain.

Finally, the third arm can also be used to implement multiplex CARS schemes^[35–37] by taking advantage of the inherently broadband pulses generated by the HNLF. Multiplex CARS uses two synchronized pulses, a narrowband (typically 10 cm^{-1}) pump, providing spectral resolution, and a broadband Stokes pulse, enabling the detection of a complete vibrational spectrum without wavelength tuning. Current state-of-the-art systems for broadband CARS start from a Ti:sapphire oscillator, with the pump pulse generated by spectral filtering and the Stokes obtained by supercontinuum generation in a photonic crystal

Figure 7. Multiplex coherent anti-Stokes Raman scattering (CARS) spectrum of cyclohexane acquired with the broadband Stokes pulse shown in Fig. 6(d). Pump power was 50 mW, Stokes power was 10 mW and the integration time was 3 ms.

fiber. In our setup, the broadband Stokes is provided by the dispersive wave centered at 1000 nm (Fig. 6(d)), which is sufficiently broad to cover all vibrational signatures lying in the CH stretching region and carries a considerable power spectral density of 0.2 mW/nm . As a preliminary demonstration of this scheme, we acquired a broadband CARS spectrum of cyclohexane (Fig. 7). An input pump power of 50 mW, a Stokes power level of 10 mW and an integration time of 3 ms were sufficient to saturate a standard optical multichannel analyzer (Ocean Optics HR 2000). The system, when coupled to more sophisticated spectrometers, holds a great potential for quick acquisition of CARS images with a broad spectral coverage.

Figure 6. Applications of the third arm: (a) synthesis of two Stokes pulses for two-color imaging; (b) synthesis of two frequency separated Stokes pulses for frequency-modulation coherent anti-Stokes Raman scattering (CARS); (c) synthesis of a local oscillator (LO) for interferometric CARS; (d) synthesis of a broadband Stokes pulse for multiplex CARS.

Conclusions

This paper reports on the first experimental results obtained with a new fiber laser system for coherent Raman imaging, in both the CARS and the SRS configurations. The system relies on an Er:fiber femtosecond oscillator driving three amplified branches, two of which are coupled to nonlinear fibers giving highly controllable supercontinua tunable over more than one octave. Such broadband femtosecond pulses are converted with high efficiency into narrow-band, tunable, picosecond pulses by spectral compression in second-order nonlinear crystals. The system generates pump and Stokes pulses with performances comparable with those of state-of-the-art systems for CARS/SRS, but with advantages in terms of compactness, cost and versatility. In fact, the third arm can be quickly configured to provide either a second narrowband Stokes pulse to be used for NRB suppression or two-color imaging, or a broadband Stokes pulse for multiplex CARS. Experimental results, so far limited to spectroscopic tests, are quite promising in view of applications of this new source to mainstream biomedical imaging.

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