

Amplified wavelength–time transformation for real-time spectroscopy

D. R. SOLLI*, J. CHOU AND B. JALALI

Department of Electrical Engineering, University of California, Los Angeles, California 90095, USA

*e-mail: solli@ucla.edu

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Real-time spectroscopy provides invaluable information about the evolution of dynamical processes, especially non-repetitive phenomena. Unfortunately, the continuous acquisition of rapidly varying spectra represents an extremely difficult challenge. One method, wavelength–time mapping, chirps the spectrum so that it can be measured using a single-shot oscilloscope^{1–4}. Here, we demonstrate a method that overcomes a fundamental problem that has previously plagued wavelength–time spectroscopy: fine spectral resolution requires large dispersion, which is accompanied by extreme optical loss. The present technique uses an optically amplified wavelength–time transformation to beat the dispersion-loss trade-off and facilitate high-resolution, broadband, real-time applications. We show that this distributed amplification process can even be pumped by broadband noise, generating a wide gain bandwidth using a single pump source. We apply these techniques to demonstrate real-time stimulated Raman spectroscopy. Amplified wavelength–time Raman spectroscopy creates new opportunities for the study of chemical and physical dynamics in real time.

Real-time spectroscopy is a powerful tool for studying dynamic chemical and physical systems. Unfortunately, conventional spectrometers are relatively slow, and do not permit real-time measurements. Recently, a technique has emerged known as wavelength–time mapping, which uses chromatic dispersion to acquire spectra directly in the time domain^{1,5}. Inspired by photonic time-stretch analog-to-digital conversion⁶, wavelength–time mapping has been applied to infrared absorption spectroscopy of gaseous compounds^{1–4}.

Wavelength–time spectroscopy circumvents conventional spectrometers and permits real-time single-shot measurements of rapidly evolving or fluctuating spectra. The technique—chirped wavelength encoding and electronic time-domain sampling (CWEETS)—transforms the temporal envelope of a signal into its spectrum using group-velocity dispersion (GVD) to chirp the signal (that is, to map wavelength into time). Once the temporal profile is mapped into its spectral shape, the spectrum can be acquired directly in the time domain using a single detector and a real-time oscilloscope^{1–3,7}.

Unfortunately, real-time wavelength–time spectroscopy has been fundamentally limited by the high loss of dispersive elements. In a real-time measurement, signal averaging is not possible and, thus, a signal can only be dispersed so much before it falls beneath the single-shot noise floor. On the other hand, substantial dispersion is required because the amount of dispersion determines the spectral resolution in the time domain.

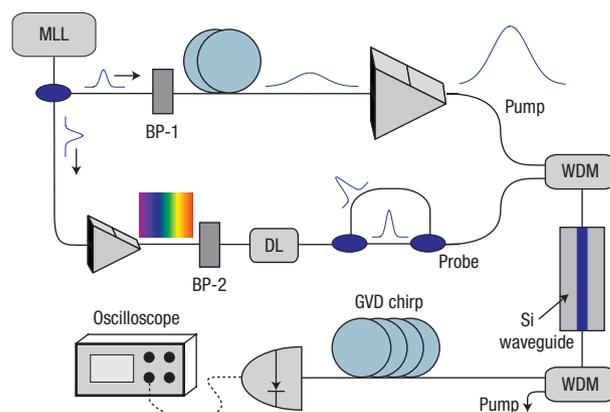


Figure 1 Schematic of the CWEETS set-up used to measure the SRS spectrum in a silicon waveguide. A mode-locked laser (MLL) serves as the master oscillator. A portion of the output is bandpass (BP-1) filtered, stretched and amplified for use as the pump. Another portion of the MLL output is spectrally broadened in an independent amplifier and carved (BP-2) for use as the probe. A delay line (DL) synchronizes the pump and probe pulses, and a copy of the probe, not synchronous with the pump, is created as a reference. Wavelength-division multiplexers (WDMs) combine and separate the pump and probe pulses at the input and output of a silicon waveguide. The scattered probe signal is then chirped in DCF and detected in real time.

The trade-off between dispersion and loss is the key limiting factor in single-shot wavelength–time spectroscopy. Furthermore, the Kramers–Kronig relations (fundamental expressions linking dissipation and refraction) impose restrictions on the dispersion-to-loss ratio⁸. In other words, dispersion is inexorably linked to loss in passive media.

Here, we show that this problem can be solved using distributed Raman amplification directly in the dispersive medium. The amplified wavelength–time transformation overcomes the fundamental trade-off between dispersion and loss. We simultaneously use the medium's linear dispersion and one of its nonlinear properties—Raman gain—to overcome the dispersion-loss limitation, and raise weak signals above the detection noise floor. We also show that broadband amplification can be achieved using incoherent pump light. We demonstrate the utility of the amplified wavelength–time transformation in real-time stimulated Raman spectroscopy, a nonlinear technique suitable

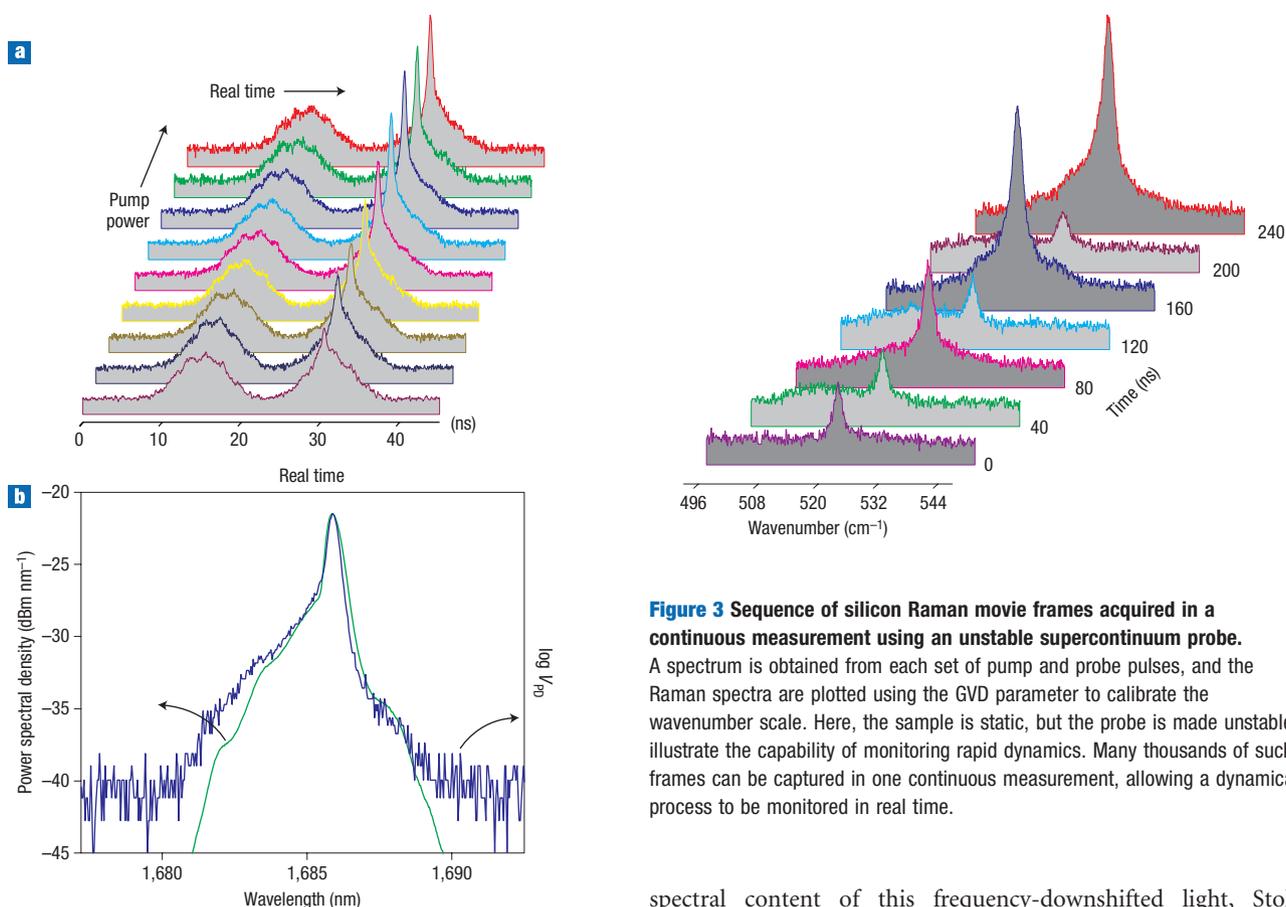


Figure 2 Single-shot SRS spectra of silicon measured with CWEETS.

a, Single-shot measurements of silicon's Raman spectrum for different pump power levels. The pump peak power ranges from roughly 15 W to 110 W. The reference pulse, which does not contain the silicon gain line, precedes the Raman probe. The bottom axis shows the calibrated wavelength scale. At high pump power levels, two-photon absorption and free-carrier absorption reduce the overall level of the Raman probe slightly; however, the reference pulse, which is not synchronized with the pump, is not affected. **b**, Comparison of a single-shot CWEETS spectral measurement (blue line) with a time-averaged measurement by a conventional optical spectrum analyser (green line). The frequency scale of the CWEETS trace is calibrated using the nominal GVD value of the dispersive medium. The spectra match closely around the Raman gain line, but begin to separate at low levels as a result of the noise level in the single-shot measurement. V_{pd} is the voltage detected at the photodetector.

for high-resolution studies of molecular dynamics. This demonstration represents not only the first application of the CWEETS technique to Raman spectroscopy, but also the first application of an amplified wavelength–time transformation for detection of weak spectroscopic signals. For clarity, we point out that Raman scattering plays two independent roles in our experiments: broadband Raman gain amplifies the weak spectroscopic signal during the wavelength–time transformation, and the signal itself is the Raman spectrum of the sample under test.

Among spectroscopic methods, Raman scattering has long been an important tool for identification and characterization of chemical species⁹. In its most commonly practised form, intense 'pump' light is passed through a chemical medium and a minute fraction is spontaneously scattered to lower frequencies by molecular vibrations and rotations. The

Figure 3 Sequence of silicon Raman movie frames acquired in a continuous measurement using an unstable supercontinuum probe.

A spectrum is obtained from each set of pump and probe pulses, and the Raman spectra are plotted using the GVD parameter to calibrate the wavenumber scale. Here, the sample is static, but the probe is made unstable to illustrate the capability of monitoring rapid dynamics. Many thousands of such frames can be captured in one continuous measurement, allowing a dynamical process to be monitored in real time.

spectral content of this frequency-downshifted light, Stokes radiation, corresponds to specific bonds and functional groups and, thus, serves as a unique molecular fingerprint. A much larger amount of Stokes light can be produced if the inelastic process is stimulated by seed radiation at the Stokes wavelength¹⁰. This nonlinear effect—stimulated Raman scattering (SRS)—has been used to create Raman lasers and amplifiers¹¹, and can also be used for spectroscopy^{12,13}. Stimulated Raman scattering requires much shorter integration times, making time-resolved, single-shot studies possible. Furthermore, stimulated Raman linewidths tend to be sharper than those of the spontaneous variety¹⁴, an advantage for differentiating similar species. Fluorescence contamination is also less significant because of the directional selectivity of SRS.

Recently, a pump–probe technique capable of recording high-resolution time-resolved stimulated Raman spectra has been reported^{15–17}. In this technique, two pulse trains derived from the same ultrashort laser source serve as the pump and probe. One train is spectrally filtered to produce picosecond pump pulses—a compromise between peak power and spectral resolution—and the other is spectrally broadened in a nonlinear medium to serve as the broadband, time-resolving Stokes probe. If a chemical reaction is activated by an optical trigger pulse, the Raman spectrum can be measured after a precise time interval by controlling the relative path lengths between the trigger pulse and the Raman probe. Then the temporal evolution can be reconstructed by repeating the process for different relative path lengths. This method has been used to measure Raman spectra with extremely fine temporal resolution, providing new insights into ultrafast chemical processes^{15–17}.

Here, we also encode the stimulated Raman spectrum onto a supercontinuum probe pulse using a narrow-band pump pulse, but perform real-time measurements using the CWEETS method. Once the temporal profile is mapped into its spectral

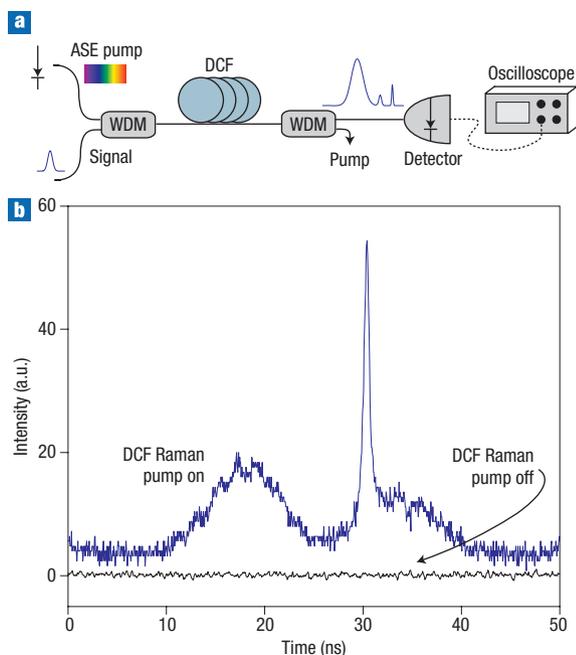


Figure 4 Demonstration of the amplified wavelength–time transformation in spectroscopy. **a**, Schematic of the set-up. Amplified spontaneous emission is used as a pump source for distributed Raman amplification of a single-shot spectroscopic signal as it is simultaneously chirped for time-domain detection according to the CWEETS method. **b**, Plot of the output. The reference pulse, which does not contain the silicon gain line, precedes the probe pulse. The amplification raises the signal, which is otherwise invisible, well above the measurement noise floor. The calibrated wavelength scale for each pulse matches that of Fig. 2b.

shape, the stimulated Raman spectrum is sampled directly in the time domain using a single photodetector and an ultrafast single-shot digital oscilloscope. The present method eliminates the need for a conventional spectrometer and allows real-time acquisition of Raman spectra at the pump–probe repetition rate. During the wavelength–time mapping process, we use broadband distributed amplification within the dispersive medium to lift otherwise undetectable signals above the measurement noise floor. Using this method, many thousands of sequential Raman snapshots of a dynamical process can be directly recorded and processed in real time.

To begin the proof of concept, we demonstrate the CWEETS technique with Raman spectroscopy in a silicon waveguide using the experimental set-up shown in Fig. 1. The vibrational Raman spectrum of silicon has been well studied using standard methods^{18,19}, and SRS has been used to construct silicon Raman lasers^{20,21} and amplifiers^{22–24}. In the present work, supercontinuum probe pulses centred at $\sim 1,686$ nm stimulate Raman scattering from pump pulses (synchronized with the probe) at 1,550 nm inside a silicon waveguide. As the pump pulses are much longer than the probe pulses, the Raman gain is essentially constant in time. This encoded pulse is then chirped in a module of dispersion-compensating fibre (DCF; low-loss, highly dispersive commercial fibre designed to compensate for anomalous dispersion in long-haul optical-fibre networks), and detected in the time domain using a photodetector and a real-time oscilloscope.

Using this configuration, we measure the SRS spectrum of silicon in real time for different pump power levels (see Fig. 2a). Note that, in general, net Raman gain is not required for SRS

measurements. Figure 2b directly compares the CWEETS-measured single-shot spectrum to the time-averaged result obtained by a traditional optical to analyser. Clearly, the data agree well around the Raman line, validating the technique. In some situations, it may be necessary to correct for the dispersion slope of the DCF to correctly calibrate the wavelength scale¹; however, in the present case, this was not required. The difference at low signal levels illustrates that post-amplification may be needed to raise the weak spectroscopic signals above the detection noise level, an issue that we discuss in more detail below.

To emphasize the real-time capabilities of this technique, we also measure the temporal evolution of a dynamic process. If the supercontinuum pulse energy is increased above a threshold level, its amplitude becomes unstable and varies randomly from pulse to pulse²⁵. This fluctuation is reflected in real-time SRS measurements using the unstable supercontinuum pulses as the probe, as presented in Fig. 3. Although in the present situation the Raman gain spectrum itself remains unchanged with time, this demonstration illustrates that the CWEETS technique captures transient effects and can be used to monitor dynamics in a real-time continuous measurement, with successive pulses representing a sequence of Raman movie frames. In the demonstration shown in Fig. 3, the dead-time between Raman snapshots is a mere 40 ns. This capability could be used, for example, to monitor a biochemical process with a continuous single-shot measurement or to conduct high-speed Raman microscopy.

The detection of weak signals presents a significant challenge in spectroscopy, especially when averaging cannot be used. As described above, using GVD to chirp the signal complicates matters further because large dispersion is accompanied by extreme loss. Although optical amplification of the signal offers a possible solution to this problem, traditional optical amplifiers are generally only available for a limited number of restricted wavelength bands. On the other hand, Raman amplifiers are not fundamentally tethered to specific wavelengths, but can operate wherever suitable Raman pumps and gain media are available.

Distributed Raman amplification²⁶ is particularly well suited to the CWEETS technique because it simultaneously exploits the linear and nonlinear properties of the dispersive medium. In DCF, for example, it has been shown that fairly broadband signals can be uniformly amplified and simultaneously dispersed using multiple Raman pump lasers spaced over suitable wavelength intervals²⁷. So far, such distributed amplification has not been applied to wavelength–time spectroscopy. For detection of weak signals, the amplified wavelength–time transformation can be used not only to avoid loss in the dispersive element, but even to produce net gain.

Interestingly, coherent pumping is not always necessary to generate a useful amplified wavelength–time transformation. If the noise floor of the detector or digitizer is the limiting factor for the measurement, it is possible to improve the effective detection threshold using incoherently pumped Raman amplification. The advantage of this approach is that a single broadband source of intense incoherent light, such as amplified spontaneous emission (ASE) from a fibre amplifier or superluminescent diode, can be used to produce uniform Raman gain in lieu of multiple pump lasers. Although the noise of the incoherent pump is a concern, it has been shown recently that incoherent pumping can provide low-noise Raman amplification for long-distance telecommunications with minimal relative intensity noise transfer from the pump to the signal^{28,29}.

We demonstrate the utility of an incoherently pumped amplified wavelength–time transformation in spectroscopy by amplifying a weak stimulated Raman pulse from the silicon waveguide directly in DCF using a broadband (continuous-wave)

ASE pump, as shown in Fig. 4. The signal is combined with the ASE pump and amplified by the Raman gain of DCF while being simultaneously dispersed according to the CWEETS prescription. Although a detailed analysis of pump noise transfer remains to be performed in the context of spectroscopy, the amplification allows an otherwise undetectable signal to be acquired without noticeable degradation.

In summary, we have reported a new experimental technique for real-time spectroscopy. This method features direct digital acquisition in the time domain by means of an amplified wavelength–time transformation, overcoming a fundamental limitation that has plagued previous implementations of chirped real-time spectroscopy. Our results represent the first application of an amplified wavelength–time transformation and the first application of the CWEETS technique to Raman spectroscopy. These methods can be used, for example, to monitor biomolecular dynamics at intervals set by the pulse repetition rate in a continuous real-time measurement. Finally, we point out that the CWEETS concept, the amplified wavelength–time transformation and general post-amplification of spectroscopic signals have broad utility and can also be applied to microscopy and other varieties of spectroscopy.

METHODS

The master oscillator used to generate the pump and probe pulses is a mode-locked erbium-doped fibre laser producing near-transform-limited picosecond pulses at approximately 1,550 nm with a repetition rate of 25 MHz (average power ~ 2 mW). To generate the pump pulses, the oscillator pulses are pre-stretched to approximately 50 ps, spectrally filtered (3-dB bandwidth ~ 0.5 nm) and amplified to a desired level in a fibre amplifier. A supercontinuum Stokes probe is generated directly within the gain fibre of a separate fibre amplifier using a portion of the oscillator output as the seed²⁵. The supercontinuum pulses are bandpass filtered at $\sim 1,685$ nm ($\Delta\lambda = 10$ nm), synchronously combined with the pump pulses using a wavelength-division multiplexer (WDM) and coupled to a silicon waveguide (mode area $\sim 7 \mu\text{m}^2$). The coupled average probe power is $\sim 100 \mu\text{W}$. The maximum coupled peak pump power is ~ 110 W. At high peak power, the pump spectrum broadens within the waveguide; however, for the power levels used in this work, it always remains less than the spontaneous Raman linewidth of silicon (~ 1 nm), permitting subnanometre Raman resolution.

At the output of the waveguide, the pump is removed using another WDM, leaving only the supercontinuum encoded with the stimulated Raman spectrum of silicon. The DCF fibre used to chirp the signal produces approximately $-1,300 \text{ ps nm}^{-1}$ of GVD at 1,550 nm and has a measured loss of ~ 10 dB at the probe wavelength. Dispersion-compensating fibre is an excellent medium for this application because it has a high dispersion-to-loss ratio, roughly twice that of standard single-mode fibre (SMF-28). The stretched pulses are then delivered to an amplified photodetector whose electrical output is captured by a real-time 20-gigasample-per-second oscilloscope (equivalent to ~ 26 samples nm^{-1}). A delayed copy of the supercontinuum probe (not synchronized with the pump) is also routed through the waveguide for reference.

For the noise-pumped amplified wavelength–time transformation, continuous-wave ASE (~ 1 W) is produced by a fibre amplifier with no input. Its spectral content is more than sufficient to uniformly amplify the signal pulse given the Raman response of DCF. Fortuitously, DCF has a much higher Raman gain coefficient than standard single-mode fibre²⁷, presenting another advantage for this application.

As described, the CWEETS technique is based on the concept of wavelength–time mapping: when a signal is chirped by a large GVD, its temporal envelope disperses into its spectral profile. To use an analogy, GVD temporally separates the frequency components of a signal like a chromatograph temporally separates the chemical constituents of a mixture. In the present case, the frequency scale of this time-domain signal is calibrated using the GVD value and a known spectral feature as an absolute wavelength reference point. The CWEETS concept of wavelength–time mapping can be demonstrated mathematically by examining the role of dispersion on the Fourier components of a hypothetical signal:

$$f'(t) = \int \tilde{F}(\omega) e^{(-i\beta_2 z \omega^2/2)} e^{i\omega t} d\omega$$

where ω is the angular frequency, t is time, $\tilde{F}(\omega)$ is the Fourier transform of the signal, $f'(t)$ is the temporal profile of the dispersed signal, and $\beta_2 z$ is the GVD produced by a linearly dispersive medium of length z . Because we are concerned with the temporal envelope of the signal, this expression can be written as

$$|f'(t)| = \left| \int \tilde{F}(\omega) e^{(-i\beta_2 z/2)(\omega - (t/\beta_2 z))^2} d\omega \right|$$

If the GVD is large, we can apply the stationary-phase approximation to simplify the integral:

$$|f'(t)| \propto \left| \tilde{F}\left(\frac{t}{\beta_2 z}\right) \right|,$$

which demonstrates that the temporal profile of the dispersed signal assumes the shape of its spectrum when sufficiently dispersed. The better-known spatial analogue of this concept is described by Fraunhofer diffraction theory, which states that the far-field diffraction pattern of an aperture is given by the Fourier transform of its transmittance function.

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