Sapphire SF: Low-Noise Ultra-Narrow Bandwidth Performance Delivers Superior Raman Spectroscopy Results

Based on field-proven optically pumped semiconductor laser (OPSL) technology, recent data confirm that Coherent Sapphire SF lasers at 488 nm and 532 nm (and other visible wavelengths) are ideal excitation sources for high-resolution Raman spectroscopy.

Introduction

Raman spectroscopy is a powerful analytical tool because, like Fourier Transform Infrared (FTIR) spectroscopy, it can yield well-resolved spectral signatures based on fundamental vibrations, thus enabling quantitative measurement of many different chemical species in the solid and liquid phase. But unlike FTIR that operates in the mid-IR, Raman spectroscopy can be performed at visible wavelengths. This significantly simplifies its implementation in both laboratory and process monitoring applications. Nonetheless, Raman spectroscopy has not achieved the wide-acceptance of FTIR and some other types of optical spectroscopy. One reason for this has been the limitations of the available lasers required to provide the intense monochromatic excitation required for successful Raman spectroscopy. In this whitepaper we briefly examine these limitations, and then present a relatively new type of ultra-narrow bandwidth laser for Raman spectroscopy – the Coherent Sapphire SF series. Based on Coherent's unique and field-proven optically pumped semiconductor laser (OPSL) technology, we show why these lasers are well-suited for Raman spectroscopy, eliminating many of the drawbacks of traditional gas, crystal, and diode lasers. We then illustrate this discussion with some sample Raman spectra recorded with these lasers – spectra that exhibit the desirable characteristics of high resolution and low background noise, together with high sensitivity, i.e., short data acquisition times.

Traditional Raman Laser Excitation

Although inelastic Raman scattering was discovered many decades ago, it was not until the invention of the laser that Raman spectroscopy became practical for typical samples. Because Raman spectroscopy measures wavenumber shifts in scattered light, resolved spectra can only be obtained with a monochromatic source. The Raman effect is also very weak – maybe only 1 in 10^8 - 10^{10} excitation photons are Raman scattered – so an extremely bright source is also required to produce sufficient signal to noise. The invention of the laser finally met this basic need.

Initially, Raman spectroscopy also required a cumbersome double or even a triple monochromator to eliminate Rayleigh scattered laser light. In addition, long data acquisition times were necessary as the slit was slowly scanned over the desired wavelength range. But these practical drawbacks were eliminated by the near-simultaneous introduction of holographic narrowband filters for blocking Rayleigh scattered light, and cooled CCD (and now s-CMOS) arrays for multiplex wavelength detection. While these advances in wavelength filtering and signal detection undoubtedly helped to promote the use of Raman spectroscopy, they have also served to further highlight the limitations of the available laser excitation sources.

Let us briefly review these sources and their limitations. Based on gas plasma technology, helium neon (HeNe) lasers offer the lowest cost, but only deliver output of sufficient power at one wavelength, 633 nm. And even at this wavelength, the power is typically less than 25 mW, unless the plasma tube is impractically long. These lasers also emit broadband background light that shows up as problematic background in the dispersed Raman spectrum. And because they use a plasma tube, most of their electrical input power is converted to heat, causing thermal management challenges in compact setups and OEM instruments.

Also based on plasma tubes, argon and krypton ion lasers offer a range of fixed wavelengths, e.g., 351, 458, 488, and 514 nm. They can deliver 100's of mW or more at several of these wavelengths. But they are bulky, delicate and produce massive amounts of waste

heat. And like the HeNe laser, the plasma tube generates broadband background light. Moreover, obtaining high output powers requires both a cooling water supply and a special power outlet.

Crystal based diode pumped solid state (DPSS) lasers (e.g., Nd:YAG and Nd:YVO_4), can deliver high beam quality and power stability. But the physics of the laser medium limits these lasers to just a few wavelengths, mainly 1064 nm and 532 nm. Also, obtaining narrow-bandwidth, low-noise operation raises the complexity and cost of these lasers. And because of thermal lensing in the laser crystal, adjusting the output power usually causes changes in the output beam quality and shape.

Diode lasers offer the advantage of solid state construction – they are compact, reliable, and efficient. But, in their raw form they are completely unsuitable for Raman spectroscopy because their wavelength characteristics are unstable and their output beam is highly divergent and asymmetric. They are also prone to damage from back reflections. Several diode laser designs have been developed for telecom applications that include a monolithically integrated wavelength control element. Examples include the distributed feedback (DFB) device, the distributed Bragg reflector (DBR) and the volume Bragg grating (VBG). These have been used in some simple Raman applications but they are not best choice to obtaining high resolution spectra and high signal to noise ratios. Their limitations include their limited spectral brightness, poor beam quality, high unit-to-unit variations, wavelength drift and instability. In addition their mode spectrum often varies dynamically and they also emit substantial broadband amplified spontaneous emission (ASE).

So for Raman spectroscopy, diode lasers are usually incorporated in external cavity (open-resonator) designs of the Littrow or Littman-Metcalf type. These are relatively complex systems negating the size and cost advantages of diode lasers. Also, they need temperature stabilization to avoid significant wavelength drifting and their broadband amplified spontaneous emission (ASE) must be suppressed by filters. And their output stability is very sensitive to any retroreflections.

Sapphire – Field-Proven OPSL Technology

The Sapphire family of visible lasers is based on Coherent's unique, optically pumped semiconductor laser (OPSL) technology. Because they offer numerous advantages over these legacy laser technologies they already dominate many applications for visible laser light, with over 25,000 units already in the field since their introduction in 2001. The recent development of ultra-narrow bandwidth versions – the Sapphire SF series – now makes these lasers ideal sources for next-generation Raman instrumentation.

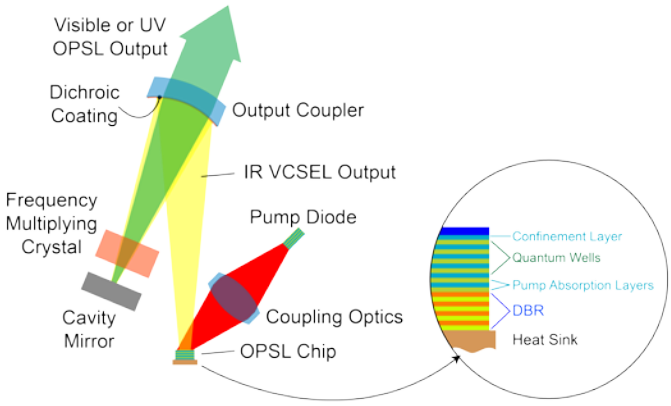

Figure 1. Schematic illustration showing the main components of an optically pumped semiconductor laser (OPSL), such as a Coherent Sapphire.

Figure 1 schematically illustrates some of the main elements of an OPSL. Pump light from a direct coupled single emitter diode laser is re-imaged into the front surface of the OPS chip. This monolithic III-V semiconductor chip contains layers of tertiary quantum wells (InGaAs) alternated between binary (GaAs) layers. The pump energy leads to population inversion and recombination in the quantum wells, which emit at a near-IR wavelength determined by the stoichiometry and physical dimensions of the quantum well structures. These aspects can be changed to scale the laser wavelength and thus support different application needs. Behind these absorption/emission layers are several alternating high index and low index layers that act as a low-loss DBR (Distributed Bragg Reflector) mirror.

The output coupler in an OPSL is an external dielectric mirror. This enables the laser cavity, and hence output beam characteristics, to be tailored at will. Also, this allows access to the intracavity beam, simplifying placement of a frequency-doubling (SHG) crystal within the resonator, which efficiently converts the near-IR output of the VCSEL to a visible wavelength, e.g., 976 nm → 488 nm, or 1064 nm → 532 nm. Yet the entire OPSL laser head can be scaled and mounted on a small block, delivering a size advantage for OEM applications, as well as excellent short-term and long-term stability. Specifically, the Sapphire SF series of ultra-narrow bandwidth lasers can deliver up to 150

mW of output from a laser head measuring only 125 x 70 x 34 mm (4.9 x 2.8 x 1.3 in.) – see figure 2.

Figure 2. High efficiency and a compact design mean that a Sapphire SF laser can produce up to 150 mW of output from a laser head measuring only 125 x 70 x 34 mm (4.9 x 2.8 x 1.3 in).

The OPSL emits over a narrow range around a center wavelength. This range supports many longitudinal modes because of the short cavity length. In a typical Sapphire series OPSL, a birefringent filter (BRF) is inserted inside the laser cavity to stabilize and limit the bandwidth to a few modes – see figure 3. The typical Sapphire bandwidth is ideal for many situations, even for some Raman applications. But high-resolution Raman spectroscopy needs a narrower linewidth. The new family of Sapphire SF lasers meets this need by also incorporating an additional high finesse frequency selective element inside the cavity to constrain the output to a single longitudinal mode, resulting in a linewidth of < 1.5 MHz.

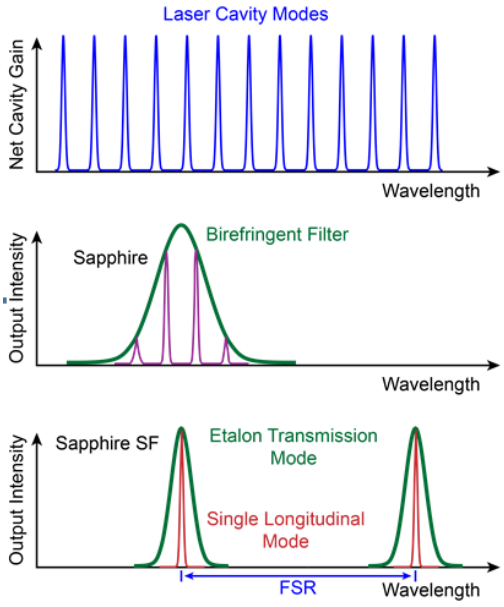

Figure 3. An additional frequency-selective element is incorporated within the Sapphire SF cavity in order to constrain laser operation to a single longitudinal mode, resulting in an output linewidth <1.5 MHz.

Why Sapphire SF for Raman spectroscopy

The construction and output characteristics of Sapphire SF lasers lead to several significant advantages for Raman applications, including:

High Spectral Purity. Several legacy laser technologies (e.g., ion, HeNe, diode) produce background, non-laser emission across a broad wavelength region, including longer wavelengths where the Stokes-shifted Raman lines are detected. This can cause an elevated background and corresponding S/N noise problems, and often necessitates filtering the laser beam with one or more narrow-bandpass filters. In contrast, the OPSL technology used in Sapphire SF lasers is completely free of this problem, which is one of the reasons for the high S/N and short acquisitions times for the sample Raman spectra shown here.

Narrow Linewidth. The resolution in a Raman spectrum is a convolution of the linewidth of the laser, the resolution of the spectrometer/CCD combination, and spectral broadening effects in solid and liquid samples. With Sapphire SF lasers, their stable ultra-narrow bandwidth (<1.5 MHz) ensures this is NEVER the limiting factor, and supports the acquisition of high-resolution Raman spectra – see figures 6 and 7.

Superior Power Stability and Flexibility. Sapphire SF lasers deliver superior power stability thanks to the inherent stability of OPSL technology, together with automated stabilization loops. Indeed, the figure below shows how the laser's stable, low-noise output is completely unaffected by even large changes in ambient temperature (see figure 4). And, because their active gain medium is a thin semiconductor disk that is efficiently cooled from its rear surface, Sapphire SF lasers do not suffer from the thermal lensing issues that limit the performance of DPSS and other solid state lasers to a narrow power range. As a result, the output power of Sapphire SF lasers can be varied from 10-100% of maximum with no effect whatsoever on beam pointing or mode quality.

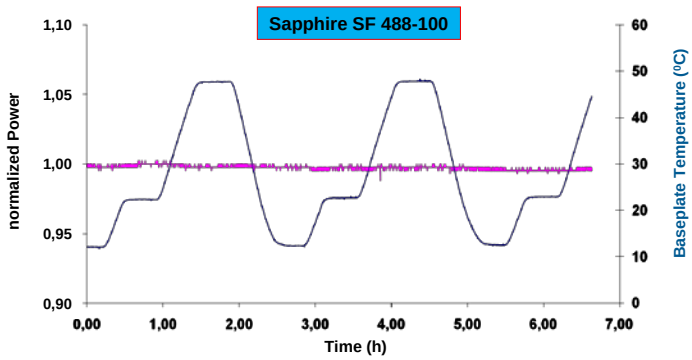

Figure 4. The output power of Sapphire SF lasers is very stable and completely unaffected by even large changes in ambient temperature.

Low Output Noise. Raman spectroscopy is characterized by low signal – 1 in 10^8 - 10^{10} or less of the incident laser photons are Raman scattered by many molecules, and only some of these photons can be captured by even the most efficient spectrometer setup. So, ultra-low laser noise is a critical requirement for Raman spectroscopy. Because they use OPSL technology, Sapphire SF lasers offer lower guaranteed output noise characteristics than any alterative excitation laser, even DPSS. And typical Sapphire SF lasers exhibit even lower noise than this specification – see figure 5.

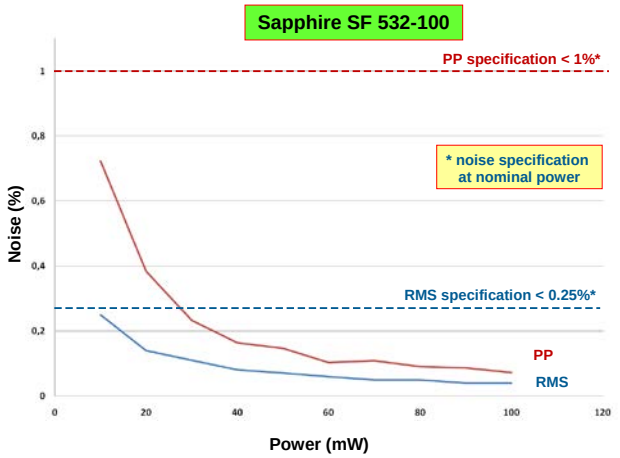

Figure 5. The output noise of Sapphire SF lasers is far below the 0.25% specification at maximum output power and at nearly every other power level.

Excellent Reliability. With the exception of low power HeNe lasers, traditional Raman excitation lasers offered only modest reliability with high replacement costs of consumables such as ion plasma tubes or pump diodes. Because Coherent is vertically integrated, including fabricating our own long-lived pump diodes, all solid-state Sapphire SF lasers have expected lifetimes > 15,000 hours.

Future Wavelength Options. Sometimes it is useful to be able to excite Raman spectra at different wavelengths, e.g., to avoid exciting resonances in mixed (e.g., bio) samples. Legacy Raman excitation lasers were limited to a few specific atomic/ionic emission lines by the laser medium. Even the notoriously problematic krypton ion laser only offers a handful of fixed visible wavelengths. But the gain medium in a OPSL like Sapphire SF can be fabricated for a target fundamental wavelength anywhere from 700 nm to 1200 nm, i.e., with a frequency-doubled output anywhere from 350 nm to 600 nm. This is the reason Sapphire lasers are offered at a growing number of wavelengths beyond the original 488 nm blue products.

Sample Raman Spectra – Liquid and Solid Samples

Liquid and Solid Carbon tetrachloride, CCl_4. The advantages of Sapphire SF lasers for high-resolution Raman spectroscopy were recently demonstrated in a study at the University Würzburg laboratory of Professor W. Kiefer [ref 1]. Specifically, a 488 nm and 532 nm laser were both demonstrated in a Raman setup that used the first stage only of a 1 meter double-monochromator equipped with a 1024 x 256 pixels cooled CCD camera. By incorporating an f = 50 mm camera lens between focal plane and CCD camera, this yielded a maximum resolution of 0.25 cm^{-1}. This was used to analyze and confirm the laser output wavelength/bandwidth characteristics. Because the system was to be used for spectra of condensed phase samples where the resolution is sample-limited, the effective slit width was then doubled to record spectra at an effective resolution of 0.5 cm^{-1}. Spectra were recorded of both carbon tetrachloride (CCl_4) and naphthalene crystal powders.

Laser powers of approximately 80 mW and 50 mW at the sample were used for excitation of room temperature and low temperature (liquid nitrogen) Raman measurements, respectively. Accumulation times were 1–30 s. No additional filters to clean the emission of the 488 nm and 532 nm lasers were used. A notch filter (488 nm) was set in front of the entrance slit of the spectrometer for the excitation of the Raman spectra of crystalline naphthalene. All other Raman spectra were taken without any notch filter.

Figure 6a shows a high-resolution spectrum of the ν_1 vibration of CCl_4 around 459 cm^{-1} obtained with a

Sapphire SF laser at 532 nm. The peaks due to different isotopes of chlorine can be clearly seen, although the resolution is limited by broadening effects in the liquid room temperature sample. A higher resolution version (6B) of the same spectrum was obtained using a sample of CCl_4 diluted in cyclohexane (30% CCl_4 by volume). Spectral narrowing due the longer ν_1 upper state lifetime can be clearly seen.

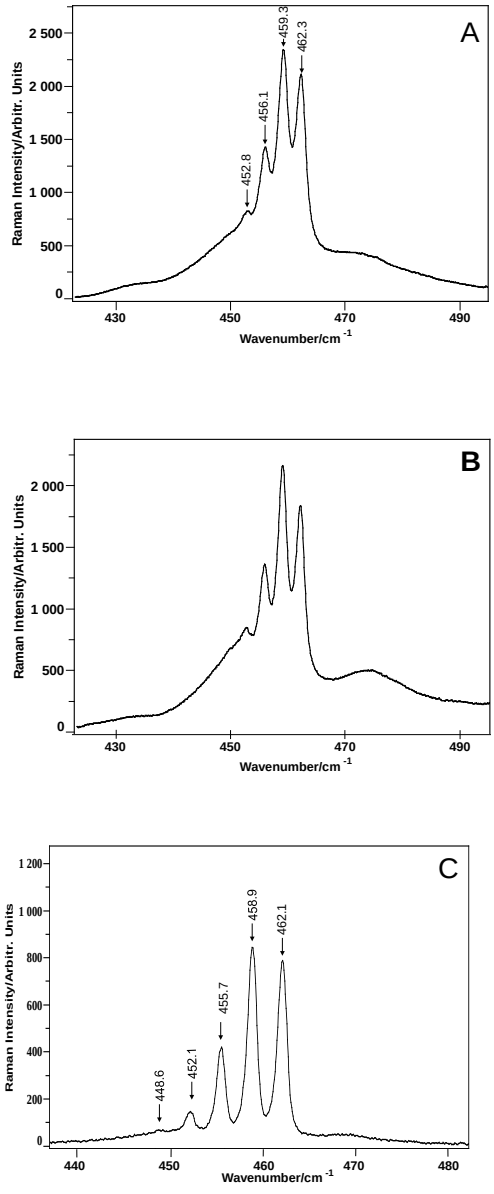

Figure 6: High-resolution Raman spectra of the ν_1-vibration of carbon tetrachloride at around 459 cm^{-1} showing the isotopic splitting of the totally symmetric vibration because of the chlorine isotopes ^{35}Cl and ^{37}Cl. (A): liquid CCl_4 (excitation with a 532 nm Sapphire SF; wavenumber values are from reference 2); (B): liquid CCl_4 (30 vol %) in cyclohexane (70 vol %), excitation with a 532 nm Sapphire SF); (C): solid CCl_4 (liquid nitrogen temperature, wavenumber values are from reference 1, excitation with a 488 nm Sapphire SF).

Many years ago, an even higher resolution Raman spectrum of this CCl_4 vibration was obtained using a 488 nm ion laser and a liquid nitrogen-cooled solid CCl_4 sample [ref 2]. Figure 6c shows identical resolution to this earlier work, but was obtained using the Sapphire SF at 488 nm with only one tenth the power of the earlier ion laser study. The excellent S/N obtained with the Sapphire SF laser, together with multiplex CCD detection means that this high resolution spectrum was obtained with a much shorter acquisition time (a few seconds) than that used in the referenced ion laser study.

Solid Naphthalene. Figures 7a and 7b show high-resolution Raman spectra of powdered solid naphthalene over the 500 – 530 cm^{-1} spectral region. Figure 7a was recorded at room temperature and Figure 7b at liquid nitrogen temperature. The Raman scattered signal was recorded at an angle of 90° to the laser beam direction. Again the data acquisition time was only a few seconds. The ability to resolve the 509.7 cm^{-1} into two separate bands in the cooled spectrum and the observation of an additional weak band to 506.1 cm^{-1} in this spectrum are clear evidence of the ability of Sapphire SF lasers to provide Raman spectra with the ideal combination of high resolution and low noise.

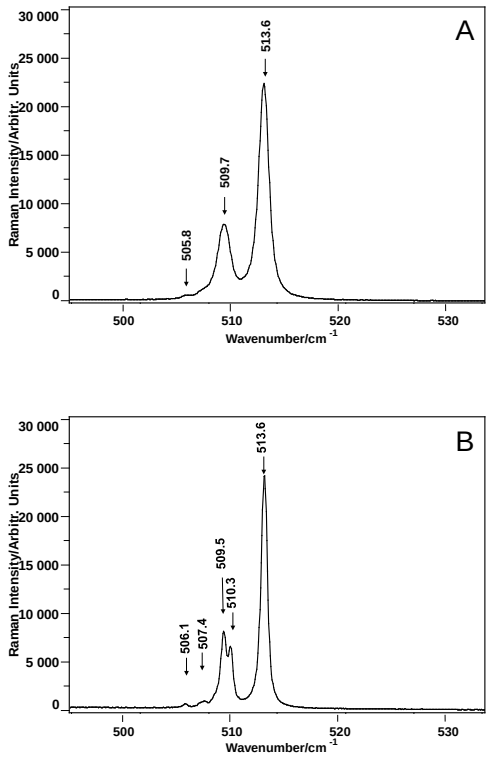

Figure 7. High-resolution Raman spectra of solid naphthalene around 510 cm^{-1} (excitation with a 488 nm Sapphire SF. (A): crystalline powder at room temperature; (B): same as (A), but at liquid nitrogen temperature.

Conclusion

High-resolution Raman spectroscopy and microscopy require a laser source with stable, ultra-narrow bandwidth output, low noise, stable output power and no broadband background. Compared to legacy lasers, Sapphire SF lasers at 488 nm and 532 nm deliver superior performance for all these key parameters. In addition, they provide high reliability, low cost of ownership, and wide power adjustability in a compact, rugged package that is ideal for both end users and OEM instrument builders.

Acknowledgement

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