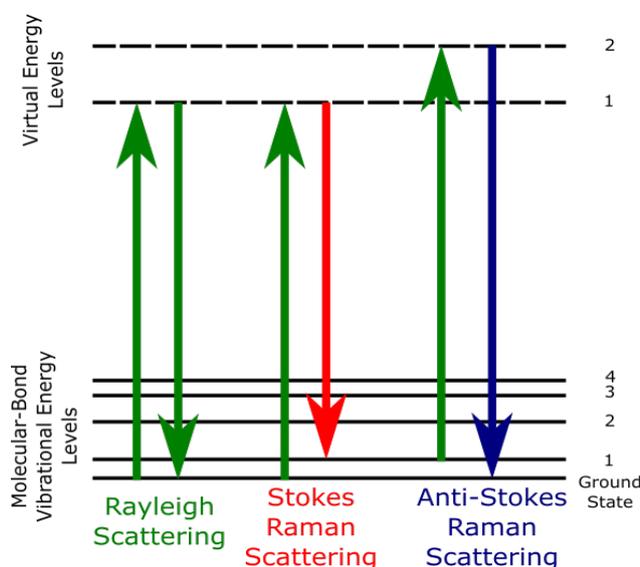


# White Paper: Use of Single Frequency DPSS lasers in Raman Spectroscopy

## Introduction:

Raman Spectroscopy is a widely used and versatile form of analysis used throughout biology, chemistry and solid-state physics (1) (2) (3). Like all spectroscopic techniques it observes how light interacts with a sample in order to understand its properties. This can then be used to identify an unknown sample, monitor how stress affects a crystal structure or look for impurities. What makes Raman different from other forms of spectroscopy is that instead of looking at light which is absorbed, emitted or elastically scattered from a sample, it looks at the light that is inelastically scattered.



*Fig. 1.* Illustrative example of Raman and Rayleigh scattering events. We can see Stokes shifts give lower energy photons whereas anti-Stokes give higher. Anti-Stokes shifts are rarer as the system needs to already be in an excited state.

## The Science of Raman Spectroscopy:

When an object elastically scatters off another object, it retains its original energy. Elastic scattering between light and matter is called Rayleigh scattering. It accounts for most scattering events seen between a light source and any given material. However, as discovered by C.V. Raman in 1928 (4), light can undergo inelastic scattering with matter. In this case the photon of light involved has a different energy before and after the scattering event. Having either lost (known as a Stokes shift) or gained (an anti-Stokes shift) energy from the matter it interacted with. This change of energy can be measured as a change in the wavelength (colour) of the light. See *Figure 1*.

The energy for this wavelength change comes from a change in the energy state of a molecular bond or bonds. Note this is distinct from an interaction where the photon is absorbed by an atom and then re-emitted at a different wavelength, which is the domain of fluorescence spectroscopy. This means the wavelength shift in the Raman scattered light corresponds directly to the current energy states of the molecular bonds in the sample (5). As these are influenced not just by the atoms involved in those bonds, but the total crystal structure and the strain the system is under, one can interpret significant useful information from its Raman spectrum that can be difficult to obtain by other means.

## **Pros and Cons:**

A significant advantage of Raman is it is non-invasive. It does not require any chemical tags or dyes to be inserted into a sample meaning often the sample is left unchanged. Raman can also be done without contacting the sample. This is helpful when identifying potentially dangerous materials.

There are, however, limitations to Raman spectroscopy. First the likelihood of a Raman scatter compared to a Rayleigh scatter is approximately 1 in  $10^6$  (6). This means the Raman signal tends to be a million times weaker than the incident light, therefore, one must filter out the much brighter Rayleigh scattered light. This is normally achieved with a sufficiently sharp dielectric bandpass, notch or edge filter.

Furthermore, to get a good signal to noise ratio an intense light source is needed. The maximum resolution of the spectrum is also dependent on the spectral bandwidth of the source. As the minimum difference in energy shift caused by two different, but very similar, molecular bond states can very small this can be critical for certain measurements. These requirements lead us to the conclusion that single frequency lasers are the optimum light source for Raman spectroscopy.

## **Lasers for Raman Spectroscopy:**

Choosing the right laser for Raman spectroscopy is critical as very different results can result from the same sample with different lasers. Firstly, the wavelength of the light has enormous impact on the results. The intensity of Raman scattered light is proportional to  $1/\lambda^4$  (7), which means a much stronger signal will be gained from using shorter wavelength light. Conversely many materials exhibit strong fluorescence when illuminated by intense light in the visible and UV (8), which can swamp the Raman signal. This means that many wavelengths from the near IR though the visible to the UV are routinely used for Raman.

At UniLasers® Ltd. our BRaMMS® technology, as well as our knowledge of many gain materials and second harmonic generation (SHG), allows us to build lasers at moderate to high powers at wavelengths throughout this spectrum. For samples liable to fluorescence we can provide high power lasers in at both 1064nm and 640nm.

Alternatively, as fluorescence often occurs in the visible, we hope soon to provide single frequency light with excellent mode quality in the deep UV at 266nm. For samples where fluorescence is not an issue, we can provide 532nm green light with up to 1W of power and will soon be supplying 320nm single frequency lasers.

Beyond wavelength, the output power, linewidth and spectral purity are all very important for Raman spectroscopy. As Raman scattering will be a weak signal, having high output power is important for getting a high signal to noise ratio. Furthermore, the spectral purity, measured as the ratio of the intensity of the main emission peak compared to any sidebands or the noise floor, is critical for resolving small stokes shifts.

As if Raman scattered light of the main emission peak is in the wavelength range of a sideband it can be swamped by the Rayleigh scattering of this wavelength. Finally, the linewidth represents the maximum resolution achievable for the system. In practice other components such as the diffraction grating used in the spectrum analyser can represent a greater limit on the resolution but for high resolution measurements not all single frequency lasers will be suitable.

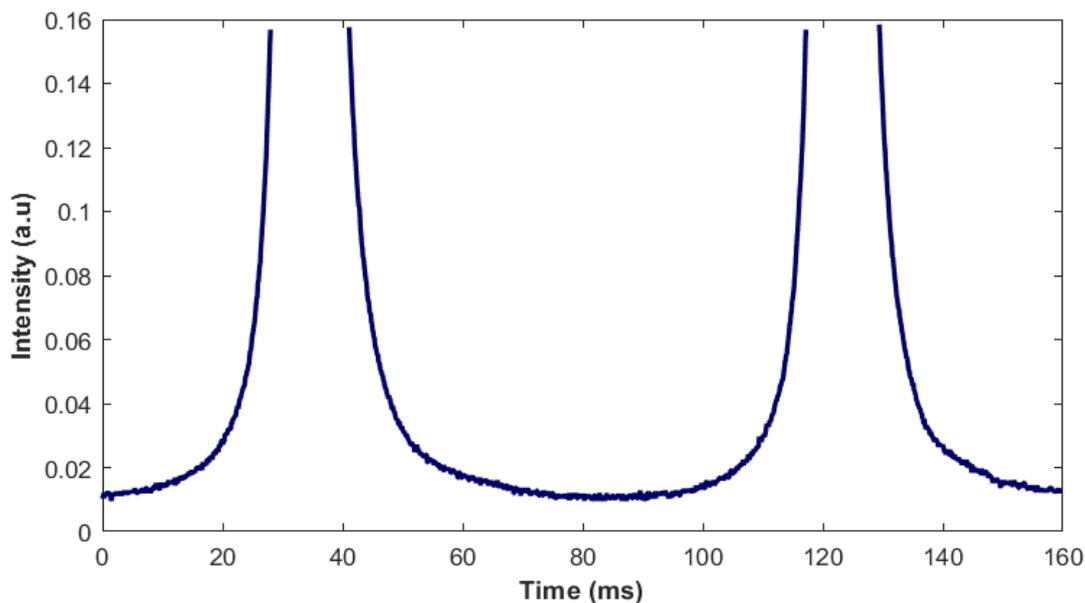


Fig. 2. Spectrum analyser trace from one of our DPSS systems, clearly showing an absence of side modes and inherent pure single frequency operation.

Three main categories of lasers are used for Raman Spectroscopy; Distributed Feedback (DFB) Diode lasers, Volume Bragg Grating (VBG) stabilised Diode Lasers, and Diode Pumped Solid State (DPSS) lasers. Whilst diode lasers often have advantages in terms of cost, efficiency and overall footprint (9), DFB lasers are limited in both power and available wavelengths (10). With only a couple of 100mWs in the red to near IR range commercially available. VBG stabilised diode lasers can operate at shorter wavelengths and higher powers however they sacrifice linewidth and spectral purity (11). This makes them unsuitable for high resolution Raman. DPSS lasers however can operate throughout the relevant spectrum with much narrower linewidths and better spectral purity (12). The compromise being a greater cost and footprint.

DPSS lasers therefore represent the high-performance laser needed for the most sensitive high-resolution Raman applications. Unlike diodes DPSS systems will operate without side bands, (see Figure 2.) a noise floor 60dB below the emission peak and with a linewidth often significantly below 1MHz.

At UniKLasers we specify our lasers to have a linewidth below 500kHz allowing you to resolve differences in Stokes shifts below  $0.02\text{cm}^{-1}$ . We can also supply up to 1.5W at 1064nm, 1W at 640nm and 532nm and soon hope to be producing up to 500mw 320nm.

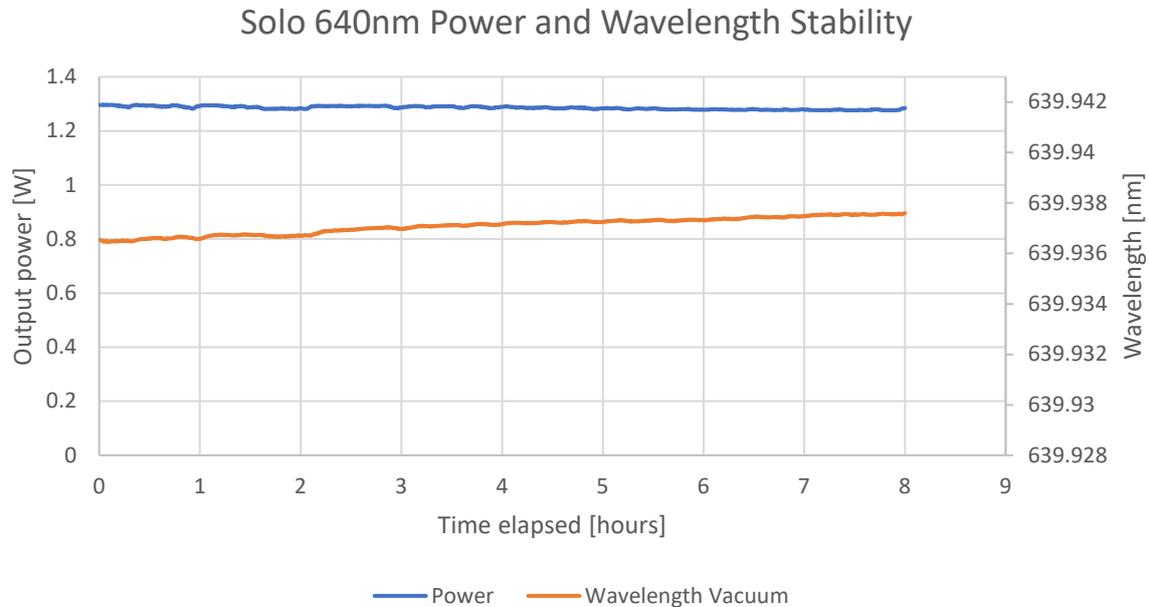


Fig. 3. Monitoring the power and wavelength of one of our 1W 640nm systems over 8 hours. The power remained within  $\pm 1\%$  and the wavelength within  $\pm 1\text{pm}$ .

With these powers much smaller signals will be detectable. Furthermore, all our lasers are stable to within  $\pm 1\%$  of the power and  $\pm 1\text{pm}$  of the wavelength over 8 hours, see *Figure 3*. This means longer measurements are still possible at high resolution, which is critical for Raman imaging applications. These all come in a shoebox size with turnkey functionality at reasonable prices.

### **Summary:**

While single frequency diode lasers have clear advantage in terms of cost, power consumption and robustness. DPSS lasers are essential for high resolution Raman analysis of difficult samples due to their narrower linewidths, better spectral purity and higher power. At UniKLasers we try to mitigate the downsides of cost, footprint and complexity often associated with DPSS lasers. Allowing for premium performance without a premium price.

### **About**

UniKLasers Ltd is a UK-based, founded in 2013, expert in CW Single Frequency DPSS lasers with a focus on mid to high output power. UniKLasers designs & manufactures single frequency lasers in a wide range of wavelengths. BRaMMS Technology® is at the

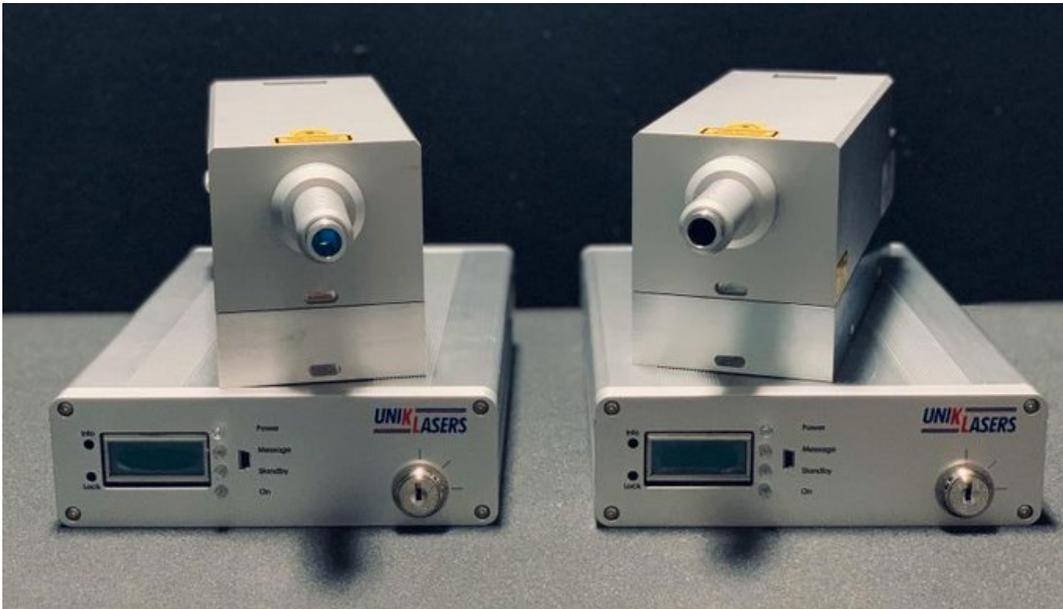


Fig. 4. Two of our 1W Solo 640 systems with integrated water-cooling block and turnkey controllers.

core of our technology platform that has established our competitive presence in the photonics market.

Lasers have excellent parameters and are particularly suited for applications that require ultra-high wavelength and output power stability, such as Spectroscopy, in particular Raman Spectroscopy, high precision metrology, Brillouin imaging, confocal microscopy, holography, semiconductor quality inspection, quantum sensing and metrology, and other high precision applications.

UniKLasers is an active player on the Quantum Technologies market. The company has a growing range of Single Frequency DPSS lasers for Quantum applications in Sensing and Metrology fields, particularly for Commercial Optical Lattice clocks and Quantum Gravitometer, such as 780.24, 698.4 and 689.4nm lasers.

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