Have I selected the right laser for my Raman experiments?

Thanks to rapid technology advancements in recent years, Raman spectroscopy has become a routine, cost-efficient, and much appreciated analytical tool with applications in material science and in-line process control for pharmaceutical, food & beverage, chemical and agricultural industries. Improvements in laser technology, detectors (CCDs and InGaAs arrays), and spectral filters (VBG-based notch filters), along with developments of new schemes for signal generation and detection, have aided Raman instrument manufacturers in overcoming the challenge of weak signals which has accelerated instrument development and market growth. In this white paper, we discuss important performance parameters to consider when selecting a laser for Raman spectroscopy experiments.

Why is the choice of laser wavelength important for Raman spectroscopy?

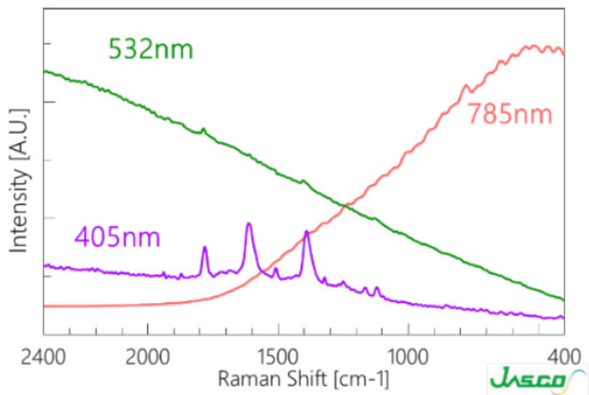
A number of different wavelengths are commonly used in Raman spectroscopy, ranging from the UV, over the visible, and into the near IR. Choosing the best illumination wavelength for a given application is not always obvious. Many variables must be considered in order to optimize a Raman spectroscopy experiment, many of which are connected to the wavelength selection.

To start with, the Raman signal is inherently very weak. It relies on the photon-phonon interaction in the sample material, which is typically a one-in-a-million event. In addition, the Raman scattering intensity is inversely proportional to the 4th order of the illumination wavelength, which means that illumination at longer wavelengths results in a decreased Raman signal.

The detector sensitivity is also dependent on the wavelength range. CCD's are commonly used for detection of the Raman signal. The quantum efficiency of these CCD devices rolls off fairly quickly beyond 800 nm. For illumination beyond 800 nm, it is possible to use InGaAs array devices, but those are associated with higher noise levels, lower sensitivity and higher cost.

The wavelength dependence of the Raman signal strength and the detection sensitivity all seem to point towards the use of shorter wavelength illumination (UV and visible) as opposed to longer wavelengths (in the near-IR). However, there is still a challenge to overcome with shorter wavelength illumination: Fluorescence emission. Many materials emit fluorescence when excited with UV-visible light, which can swamp the weak Raman signal.

Even so, the most commonly used wavelength in Raman spectroscopy is 785 nm. It offers the best balance between scattering efficiency, influence of fluorescence, detector efficiency and availability of cost-efficient and compact, high-quality laser sources. However, the use of visible lasers in the blue and green (in particular at 532 nm) is increasing.



Raman spectrum of polyimide using 3 different wavelengths. For the green and NIR the Raman signal is buried in fluorescence for 532 nm and 785 nm laser excitation. However it is easily resolved when using 405 nm.

What performance characteristics should be considered when selecting a laser for Raman spectroscopy experiments?

In addition to wavelength, there are a number of important performance parameters that should be taken into account when choosing the best laser sources for Raman experiments. Key performance parameters are: spectral linewidth, frequency stability, spectral purity, beam quality, output power and power stability, and optical isolation. In addition, the compactness, robustness, reliability, lifetime and cost structure should be considered.

Laser performance parameters	Considerations
Spectral linewidth	This sets a limit to the spectral resolution of the recorded Raman signal (i.e. how small of a difference in Stokes shift can be detected). For most fixed-grating systems, the laser linewidth should be a few 10 pm or less in order to not limit the spectral resolution of the system. However, high resolution systems may require linewidths much less than that, sometimes even less than 1 MHz.
Frequency stability	The laser line must stay very fixed in wavelength during recording of the spectrogram in order not to deteriorate spectral resolution. Typically, the laser should not drift more than a few pm over time and over a temperature range of several °C.
Spectral purity	Detecting the Raman signal normally requires a spectral purity of >60dB from the laser source (ie how well side-modes to the main laser line are suppressed). For many cases, it is sufficient if the level of spectral purity is reached at around 1-2 nm from the main peak. However, low-frequency Raman applications require a high side-mode suppression ratio (SMSR) of a few 100 pm from the main peak.
Beam quality	In confocal Raman imaging applications, it is necessary to use diffraction limited TEM_{00} beams for optimum spatial resolution. However, for probe-based quantitative Raman analysis, the requirement is not as tight. It is normally sufficient with a beam quality that allows for efficient coupling into multi-mode fibres, e.g. with 50-100 µm core diameters.
Output power and power stability	Typical laser output powers range from around 10 mW in the UV, up to several 100 mW in the near-IR. The output power requirement is related to the wavelength, the type of material(s) that will be investigated, as well as the sampling frequencies and imaging speeds.The output power of the laser should not fluctuate with more than a few %, also in a varying ambient temperature.
Isolation of laser beam	In confocal imaging set-ups in particularly, the samples can easilygenerate optical feed-back which is very well-aligned with the excitation beam. Optical feed-back can induce power and noise instabilities and, in the worst case, cause permanent damage to the laser. It is normally preferred to have an optical isolator integrated directly in the laser source itself, because careful alignment is required to achieve high stability in the output after the isolator.

Finally, the compactness, robustness, reliability, lifetime and cost structure are very important parameters to be considered in the selection of the optimum illumination source for a Raman system. Raman instrumentation has progressed into becoming a standard analytical tool in many scientific and industrial applications. Users expect to run routine experiments or process monitoring measurements for years without the need for service or exchange of the laser source. In a growing number of cases, the instrument must also operate in harsh, industrial environments.

For these reasons, most Raman systems nowadays are equipped with solid-state based laser sources rather than gas lasers. Today, compact solid-state lasers with proven operation lifetimes of several 10,000 hours which meet the most advanced optical performance requirements are available in all wavelength ranges commonly used for Raman spectroscopy.

What types of lasers are commonly used for Raman spectroscopy and how do you decide which one is best for your application?

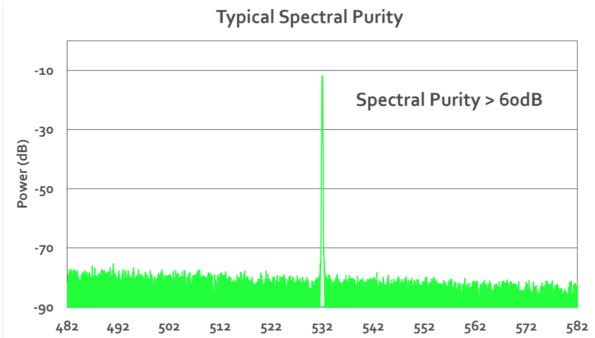
Solid-state based CW laser sources that are commonly used for Raman spectroscopy can be grouped into three categories:

i) Diode-pumped lasers: SLM (single-longitudinal mode)

ii) Single-mode diode lasers: DFB (distributed feedback) or DBR (distributed Bragg reflection)

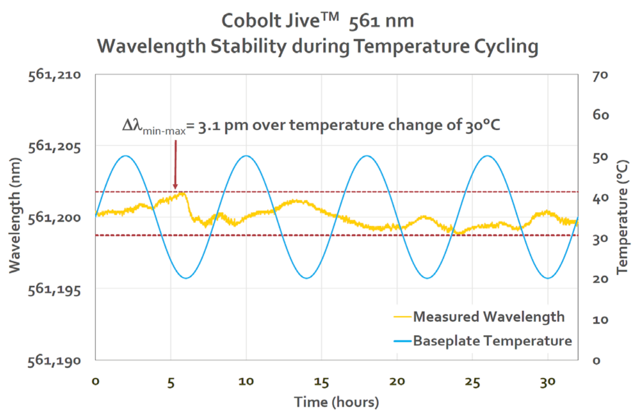
iii) VBG frequency stabilized diode lasers

These laser technologies cover different wavelength regions and have significant differences in optical performance, explained below.

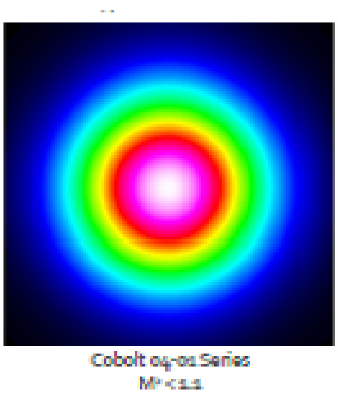


Wavelength spectrum of a Cobolt DPL (diode pumped SLM laser), the latter showing a very clean spectrum (no side-modes) below 60 dB.

i) Diode-pumped SLM lasers (DPL lasers) combined with built-in nonlinear optical frequency conversion are readily available in compact formats from the UV to the near-IR. Up to Watt power levels are achievable at 1064nm in the near IR. In the visible range, a large number of lines in the blue-green-red region (660, 640, 561, 532, 515, 491, 473, 457 nm) are available and with output powers on the scale of several hundred mW. Lower power levels are achievable in the UV, such as 10 to 50 mW at 355nm. These lasers provide excellent TEM00 beams, very precise wavelengths with low drift and a single-frequency linewidth of typically far less than 1 MHz. These lasers also offer a very high level of spectral purity with typically much greater than 60 dB SMSR up to within pm of the main peak. There may be occurrence of low level emissions at neighbouring laser lines, but they are several nanometers shifted from the main peak and therefore easily eliminated by integrating a dielectric band-pass filter. The wavelength stability is inherently excellent (see figure).



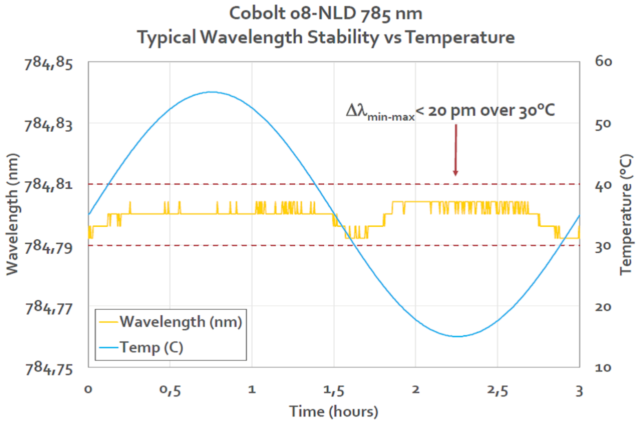
Wavelength stability of a Cobolt DPL (diode pumped laser) showing a shift < 3.1 pm over 30 °C base plate temperature change.

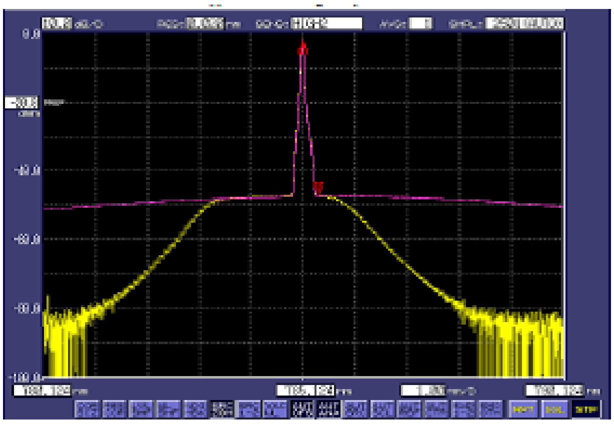


Typical TEM00 beam profile

ii) Single-mode diode lasers provide very compact and cost efficient illumination sources with single-frequency linewidth (<1 MHz) and single-transversal mode beam quality. A number of wavelengths are available in the red to near IR, with output powers up to a few 100 mW and MHz linewidth. The most commonly used wavelengths are 785, 830, 980 and 1064 nm. Side-band emission limits the SMSR of these lasers to around 50 dB, which is normally achieved at a few 100 pm away from the main peak.

iii) The third group of laser sources for Raman is VBG frequency stabilized diode lasers. In these lasers a narrow linewidth Volume Bragg Grating (VBG) element is used with a diode laser emitter to achieve narrow-line emission at wavelengths that are not available as DFB or DBR sources. It is also possible to achieve narrow linewidth emission at higher power levels by frequency locking multi-transversal mode diode lasers. Careful thermo-mechanical control and high precision alignment inside of the laser is required to achieve high stability in the output wavelength and linewidth, especially with varying ambient temperatures. Linewidths range from single-frequency emission to a few 10 pm, depending on wavelength and output power. And, as with other diode lasers, the SMSR is limited to 40-50 dB close to the main peak. However, this can be improved to 60-70 dB at 1-2 nm away from the main peak by integrating a filter.





Spectral linewidth stability in varying temperature and spectral characteristics with (yellow) and without (pink) integrated bandpass filter from a 500 mW Cobolt 08-NLD laser at 785 nm.

What are the features and benefits of Cobolt's laser technologies, and how do they serve Raman spectroscopy applications?

Cobolt serves the Raman industry with both Diode-pumped SLM lasers (DPL) and VBG-stabilized diode lasers. Both of these laser types require an extremely high level of precision in the mounting and fixation of separate optical elements. Therefore, reliable performance from such lasers can only be achieved if they are assembled with advanced optical manufacturing technology, and with proven resilience to thermal and mechanical stress. All of Cobolt's DPL lasers and VBG-stabilized diode lasers are manufactured with the company's proprietary HTCure™ technology, which relies on high temperature baking of miniaturized optics mounted with high-precision into thermo-mechanically stable and hermetically-sealed packages. This approach has proven to provide highly reliable lasers that can tolerate repeated thermal shocks over 100 oC and mechanical shocks over 60 G.

The Cobolt 08-01 Series of compact SLM and narrow-linewidth lasers is specifically designed for Raman spectroscopy applications. This product platform hosts diode-pumped SLM lasers (08-DPL) and VBG-stabilized diode lasers (08-NLD) in compact and hemertically-sealed packages. The modules have fully integrated electronics and optional optical isolators. The output beam is collimated free-space or coupled into a multi-mode or single mode fiber. Available wavelengths are 405, 457, 473, 515, 532, 561, 660, 785 and 1064 nm.

Cobolt 08-01 Series of compact SLM and narrow-linewidth lasers for Raman spectrosocpy.

About us

Cobolt is recognized as one of the leading suppliers of high performance diode-pumped lasers and laser diodes in the UV, visible and near-infrared spectral ranges. Cobolt provides a very broad coverage of compact, high performance, continuous wave lasers with reliable single-frequency or narrow-linewidth performance. Thanks to the company's proprietary HTCure™ manufacturing technology, the lasers are exceptionally robust and reliable being basically insensitive to environmental and mechanical shock. It's the inherent performance characteristics of the laser design along with the proprietary manufacturing technology which have lead to Cobolt's recognition as one of the leading laser suppliers to the Raman industry. www.coboltlasers.com