

Novel narrow linewidth 785 nm diode laser with enhanced spectral purity facilitates low-frequency Raman spectroscopy

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ABSTRACT

Raman Spectroscopy enables fast, sensitive and label-free chemical analysis of a large range of materials and has become a routine analytical tool in a wide range of material science and process-control applications.

As the Raman signal is weak it is critical that the illumination laser has a very high level of spectral purity, for efficient detection of the Raman signal. Most materials can be characterized by studying Raman shifts down to 100 cm^{-1} , but in some cases, for instance for determining the crystallinity of pharmaceutical compounds, it is required to study Raman shifts in the low-frequency regime; $<100\text{ cm}^{-1}$.

785 nm is the most common illumination wavelength for Raman spectroscopy as it offers the best compromise between Raman signal strength and fluorescence background suppression. In this paper, we present a novel design for a frequency-stabilized 785 nm diode laser using a highly reflective volume Bragg grating (VBG) element that offers not only a narrow spectral linewidth and low wavelength drift, but also a very high level of spectral purity. Using the VBG reflected light as output from the laser suppresses Amplified Spontaneous Emission (ASE) from the diode so that a very high level of side-mode suppression ratio (SMSR) in the laser output is reached within just a few cm^{-1} away from the main peak without any external spectral filtering. This enhanced spectral purity directly from the laser enables simpler, more compact and more cost-efficient detection of Raman shifts in the very low frequency range.

Keywords: Raman spectroscopy, lasers for Raman, low-frequency Raman, laser spectral purity, laser wavelength stability, Volume Bragg Gratings, frequency-locking, narrow linewidth lasers.

1. INTRODUCTION

The "inelastic scattering of light", or Raman effect, was observed in practice for the first time in 1928 by C.V. Raman for which he was awarded the Nobel Prize in 1930. It is only in the last two decades, however, that Raman spectroscopy has begun to realize its potential as an almost universally applicable analytical technique, not only in material and life science research applications, but also as a process control tool in, for instance, pharmaceutical, food & beverage, chemical and agricultural industries. Improvements in laser technology (smaller, more powerful, more robust and more wavelengths), detectors (CCDs and InGaAs arrays that allow design of instruments without moving parts), spectral filters (Volume Bragg Grating elements) and filtered probes, along with developments of new schemes for signal generation and detection, have aided instrument manufacturers in overcoming the challenge of weak signals associated with Raman spectroscopy and thereby accelerated development of much smaller, user-friendly Raman instruments.

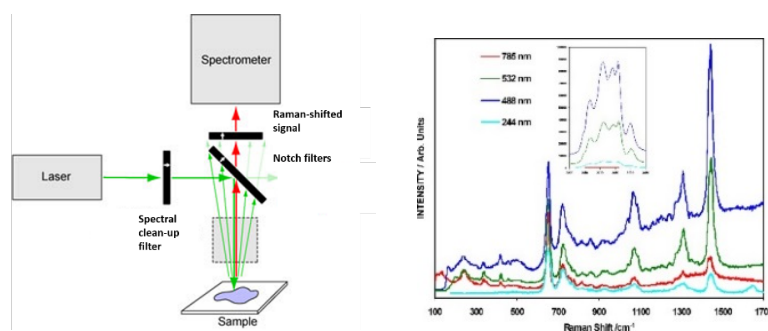


Figure 1: Basic set-up for a Raman spectrometer system and a typical Raman spectrum

Fundamentally, a Raman spectroscopy system consists of a laser, spectrometer and detector. Modern solid-state lasers offer much more compact alternatives to the previously used gas lasers and are covering a continuously increasing range of wavelengths and power levels. Another critical improvement in key components of a Raman instrument is the introduction of array-based detectors, which allow for fixed-grating configurations and eliminate the need for moving parts in the instrument. These new compact laser sources, combined with fixed-grating spectrometer configurations have enabled development of very compact and performant Raman instruments. Such portable or hand-held Raman instruments are primarily used for homeland security and forensic applications (e.g detection of explosives and bio-warfare agents). Other applications include art restoration, archaeology, drug analysis and identification of gemstones and minerals.

Another important application area for Raman instrumentation is in-line process control and product testing. For this, probe-based bench-top Raman instruments are utilized. For instance, in the petro-chemical industry Raman instrumentation is now being deployed as an alternative or complement to gas chromatographs (GCs). Another example is pharmaceutical industries, where Raman-based tools are implemented throughout the whole manufacturing chain; for new drug identification through high-through-put screening (HTS) techniques, quality inspection of raw materials, monitoring of granulation, blending and drying during processing and finally for non-invasive testing of produced tablets and gelcaps.

Raman spectroscopy is also used with confocal microscopy techniques and can in this way offer label-free high resolution imaging of chemical substance distributions. A primary advantage of Raman over fluorescence techniques in imaging applications is its capability to examine multiple different species from one single excitation wavelength. These confocal-Raman microscopes are now sensitive enough to be used also for biomedical studies, even on single-molecule levels. This capability has been enabled by developments in TERS (Tip-Enhanced Raman Spectroscopy) and SERS (Surface Enhanced Raman Spectroscopy) which have allowed Raman imaging to go beyond the diffraction limit in resolution.

The capability of confocal Raman microscopes to perform label-free characterization of biological cells and tissue in high resolution and at video-rates, combined with the development of new chemometric approaches for qualitative and quantitative Raman image analysis is paving the way for using Raman spectroscopy also for clinical diagnosis, with the potential of enabling faster identification of infectious microorganisms and improved methods for early cancer detection.

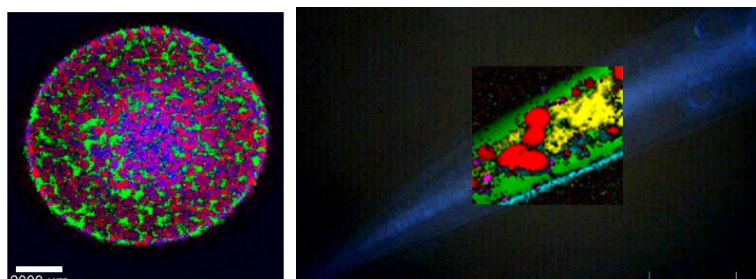


Figure 2: Examples of imaging Raman Spectroscopy applications; i) compound distribution in medical pill and ii) label-free detection and identification of micro-organisms (© Copyright Witec GmbH and Renishaw plc. respectively)

2. LOW-FREQUENCY RAMAN SPECTROSCOPY

The importance of Raman spectroscopy as an analytical tool is based on the ability to probe the unique vibrational and rotational modes of molecules in various materials. These phonon interactions induce material-characteristic frequency-shifts (Stoke-shifts) at the illumination laser wavelength that typically lay in the range from 200 - 4000 cm^{-1} . This fingerprint region is accessible with most commercial instruments and allows extracting valuable information about molecules such as aromatics, carbonates, sulphates, silicates, oxides and hydroxides within the 500-1500 cm^{-1} range, and hydrogen interactions with carbon, nitrogen and oxygen at around 3000 cm^{-1} . However, there is also a lot of interest in accessing the low-frequency Raman region (<10 cm^{-1} to 200 cm^{-1}). Raman shifts in this frequency range give access to lattice vibrations of molecular crystals and have the potential to more directly probe intermolecular interactions in solid materials. The low-frequency Raman region probes the same low-energy vibrational and rotational modes of molecular

structures as terahertz spectroscopy (300 GHz - 6 THz). The THz region of Raman spectra contain important structural information about the molecules or crystal lattices under investigation. In the pharmaceutical industry, for instance, this structural information can help to determine the crystallinity, and therefore solubility, of pharmaceuticals. Specifically, low-frequency Raman spectroscopy provides an avenue to probe polymorphic structures of pharmaceutical systems before and after tableting, as well as drug identification and quantitation for crystalline materials, both of which are critical quality attributes in pharmaceuticals [1].

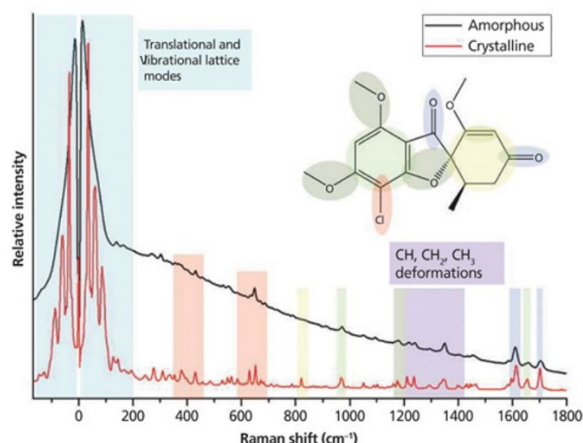


Figure 3. Example of distinguishing between crystalline and amorphous griseofulvin through low-frequency Raman spectroscopy [1].

Being able to determine the structural form of the Active Pharmaceutical Ingredients (API) is a primary concern in the pharmaceutical industry during drug development, manufacturing and quality control. APIs exhibit polymorphism, which is characterized as having identical chemical compositions but different solid-state structures that may affect the bioavailability and therapeutic index, which could lead to compromised efficiency of any final drug product [2-3].

The low-frequency Raman region for measurements of lattice phonons in pharmaceuticals has become more accessible in recent years with advances in precise optical filters and narrow linewidth lasers with a high level of frequency stability. Therefore, low-frequency region investigations in pharmaceutical products has started to transition from the academic laboratory with customized laboratory set-ups to pharmaceutical labs and production line. By equipping Raman microscopes with low-frequency Raman capability and performing multivariate analysis it has been possible to demonstrate mapping of the API distributions and crystal sizes in over-the-counter (OTC) pharmaceutical tablets as well as identification of polymorph conversions in transdermal drug delivery systems (TDDSs) [4].

Examples of other analytical applications which take advantage of probing low-energy vibrational and rotational modes through low-frequency Raman spectroscopy include; Polymer analysis (characterization of chemical composition, molecular structures, and chain orientation under mechanical deformation of polymeric material) [5], Semiconductor analysis (advanced semiconductor devices have strong signals in the low frequency region from folded acoustic and shear modes of multilayer super-lattice structures) [6] and Protein characterization.

3. LASER REQUIREMENTS FOR LOW-FREQUENCY RAMAN

In order to access the low-frequency Raman spectral range the notch filters used to separate out the Raman signal from the Rayleigh scattered light from the illumination wavelength need to be very narrow-band and provide high level of suppression. As the Raman signal, which is a photon-phonon interaction, is inherently very weak typically a Rayleigh light suppression of over 60 dB is required to record useful Raman information. Filters meeting these requirements can be fabricated by recording holograms in Photo-thermo refractive (PTR) glass through exposure of the interference pattern from a UV laser. Such Volume Bragg Grating (VBG) elements can provide notch filters with FWHM of $<1\text{cm}^{-1}$ and with a >60 dB cut-off at less than 5cm^{-1} from maximum [7].

The spectral purity requirements on the laser source for low-frequency Raman are similar to the notch filter characteristics; the laser line has to be narrow and provide a side-mode suppression ratio (SMSR) of at least 60 dB at less than 5 cm^{-1} from the main peak. The spectral linewidth of the laser 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). However, the spectral resolution of a Raman spectrometer does not only depend on the laser source. Also playing a role is the groove density of the diffraction grating, the spectrometer focal length and, in some cases, the pixel size of the detector. For most fixed-grating systems, the laser linewidth should be a few 10s of pm or less in order not to limit the spectral resolution of the system. Related to the linewidth parameter is the frequency stability, or spectral stability, of the laser. The laser line must stay very fixed in wavelength during recording of the spectrogram in order not to deteriorate spectral resolution or fall out of the notch filter spectral range. Typically, the laser should not drift more than a few pm over time and over a temperature range of several °C. In addition, the laser line has to provide sufficient output power at a suitable wavelength for the specific material under investigation.

A number of different wavelengths are commonly used in Raman Spectroscopy today, ranging from the UV, over the visible, and into the near IR (NIR). Choosing the best illumination wavelength for a given application is not always obvious. To start with, 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 rapidly decreasing Raman signal. Furthermore, the detection sensitivity is also dependent on the wavelength range. The quantum efficiency of commonly used non-cooled silicon-based CCD devices for the Raman signal detection rolls off fairly quickly beyond 800 nm. For longer wavelength illumination it is possible to use InGaAs array devices, but those are associated with higher noise levels and hence lower sensitivity. The wavelength dependence of the Raman signal strength and the detection sensitivity seem to point towards the preferred use of shorter wavelength illumination (UV and visible) over longer wavelengths (in the near-IR). However, there is a major challenge to be overcome with shorter wavelength illumination: Fluorescence emission. Many materials tend to emit a lot of fluorescence when excited with UV-visible light and this fluorescence background tends to drain the weaker Raman signal.

For some materials, the influence of fluorescence can effectively be avoided by using even shorter wavelengths in the UV spectral range. Although UV light tends to excite strong fluorescence, it is typically emitted at wavelengths above 300 nm. This opens up the opportunity to both excite and record the Raman signal below 300 nm without influence of the fluorescence, as the Raman signal is recorded very close to the illumination wavelength. However, UV lasers are still relatively costly and bulky. Other challenges with UV illumination are that the high energy of UV photons can be destructive to the sample, especially for solid phase and biological materials, and that UV-enhanced CCD cameras are costly.

With all these aspects taken into account, the resulting most commonly used wavelength in Raman spectroscopy is 785 nm. This wavelength often offers the best balance between scattering efficiency, influence of fluorescence, detector efficiency and availability of cost-efficient and compact, high-quality laser sources. In order for a laser at 785 nm to meet the requirements for low frequency Raman applications it should provide a SMSR of at least 60 dB at around 300 pm from the main peak (1 cm^{-1} corresponds to around 60 pm at 785 nm).

4. LASER DESIGN

Laser sources suitable for Raman spectroscopy at 785 nm can be fabricated from AlGaAs-based semiconductor devices. Depending on the emitter size and geometry they can be designed to emit single-transversal mode beams (lower power) or multi-transversal mode beams (higher power). Semiconductor lasers have a broad gain spectrum and typically have bandwidths of over 1 nm and with long spectral tails stretching several 10s of nm from the main peak. They can be made to emit spectrally single-mode radiation by introducing distributed wavelength selective gratings (DBR/DFB) into the structure. DBR/DFB lasers at around 780 nm are available at up to a few 10s of mW output power. As an alternative for higher power levels, it is possible to turn the broad-band emission from a semiconductor laser into narrow-band by building an external cavity with a separate wavelength-selective cavity element. In this way the stimulated emission from the laser will be frequency-locked to the spectral distribution of the feed-back from the external cavity element. A conventional way of constructing such frequency-locked semiconductor laser is to build an external cavity using a Volume Bragg Grating element (VBG), see figure 4.

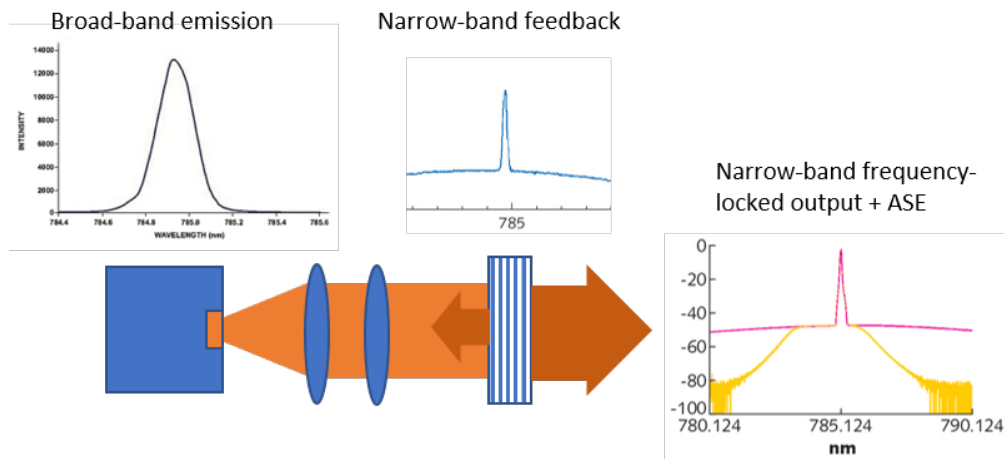


Figure 4. Basic principle for conventional frequency-locking a 785 nm edge-emitting semiconductor laser with an external VBG element. The yellow trace represents the spectral output after filtering with a standard dichroic filter.

The output beam from the 785 nm semiconductor emitter is collimated and beam shaped using spherical and cylindrical lenses and/or prism pairs in order to minimize angular distribution of the beam before going into the VBG element, which reflects a fraction of the light with a narrow spectral distribution back into the semiconductor. Typical reflectivity of the VBG element to achieve stable frequency locking is in the order of 10-40%, depending on the wavelength and gain of the semiconductor emitter.

A draw-back for both DFB/DBR and conventional VBG frequency-locked laser devices is that a fair amount of broad-band Amplified Spontaneous Emission (ASE) from the semiconductor is still emitted from the laser device. This limits the SMSR ratio to around 40-50 dB up to several nm's away from the main peak. In order for such lasers to be useful for Raman spectroscopy they have to be spectrally filtered with external clean-up filters. In the case of low-frequency Raman spectroscopy it is not enough to use standard dichroic filters with a typical bandgap of 1-2 nm, but necessary to use more narrow spectral filtering, typically by adding a second external VBG element. This additional VBG filter adds cost to the system and can be challenging to match spectrally to the specific output wavelength of the laser.

In order to overcome this draw-back we present here an alternative (patent pending) design for frequency-locking a semiconductor laser, by using a highly reflective VBG element as the wavelength selective component in the external cavity. The laser beam is instead coupled out of the cavity via a polarization sensitive mirror and the polarization state of the feedback from the VBG is controlled with an intra-cavity polarizing element. In this way, only the stimulated emission is coupled out of the cavity and the broad-band non-stimulated emission is leaking out of the VBG element. The resulting spectral purity is similar to what is achieved with an external VBG clean-up filter, but with the use of only one single VBG element. In addition to simplifying the design of the laser with maintained performance, this approach allows active control of the level of feed-back into the semiconductor laser through adjusting the polarizing element in the cavity, so that optimally stable frequency-locking can be achieved.

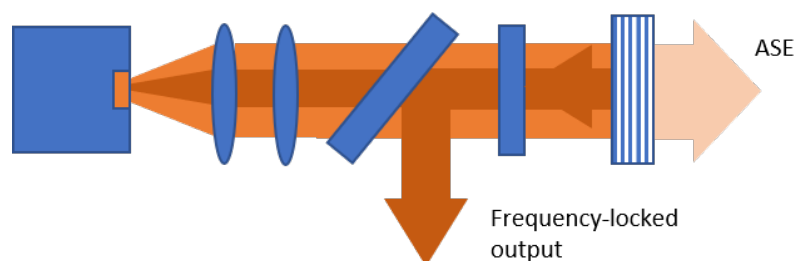


Figure 5. Frequency-locking with a highly reflective VBG element and a polarization sensitive output coupling mirror.

To demonstrate the principle, we frequency-locked a high power multi-transversal mode 785 nm edge-emitting semiconductor laser. The emitter size was 100 μm and the maximum rated output power was 2W. The output multi-transversal beam was collimated to a size of 1.6 x 1.2 mm.

All optical elements were assembled on a single temperature-controlled platform using Cobolt's proprietary HTCure™ technology with high-temperature cured adhesives to ensure robust and precise alignment of the cavity components as well as high level of thermo-mechanical stability and insensitivity to ambient conditions. An optical isolator was integrated into the laser design to ensure insensitivity to optical feed-back. Finally, the laser cavity assembly along with electronics boards for driving and control of the laser was integrated into a single-unit housing measuring 128x40x40 mm in size.

5. RESULTS

In all the following measurements of the laser's spectral characteristics the output power was set to 400 mW in a free-space beam. The measurements were recorded using a Yokogawa AQ6370 optical spectrum analyzer.

Firstly, the side-mode suppression ratio of the laser was measured, momentarily as well as monitored over time and while cycling the baseplate temperature of the laser over 15-55 °C in order to evaluate the stability of the frequency-locking. The resulting SMSR was >64 dB at ± 300 pm (corresponding to ± 5 cm^{-1}) and >74 dB at ± 1 nm from the main peak. The SMSR showed a high level of stability over time and in temperature cycling.

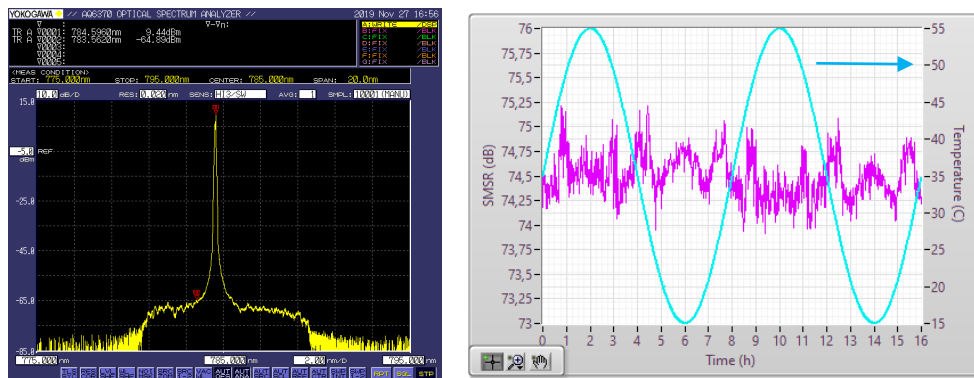


Figure 6. Laser spectrum and measured SMSR during temperature cycling of the laser baseplate

Secondly, the linewidth of the laser was measured and also monitored over time and temperature cycling. The linewidth (FWHM) remained <31 pm (corresponding to 0.5 cm^{-1}) in temperature cycling and <27 pm at constant temperature.

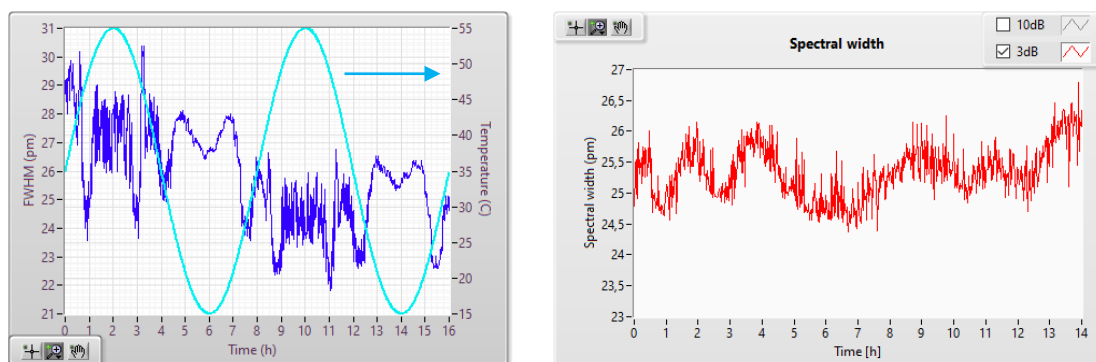


Figure 7. Measured linewidth (FWHM) during temperature cycling of the laser baseplate and at 35 °C constant temperature.

Finally, the wavelength stability of the laser was measured. The measured wavelength drift was <4 pm over 14 h at constant temperature and < 17 pm when cycling the laser baseplate over 15-55 °C.

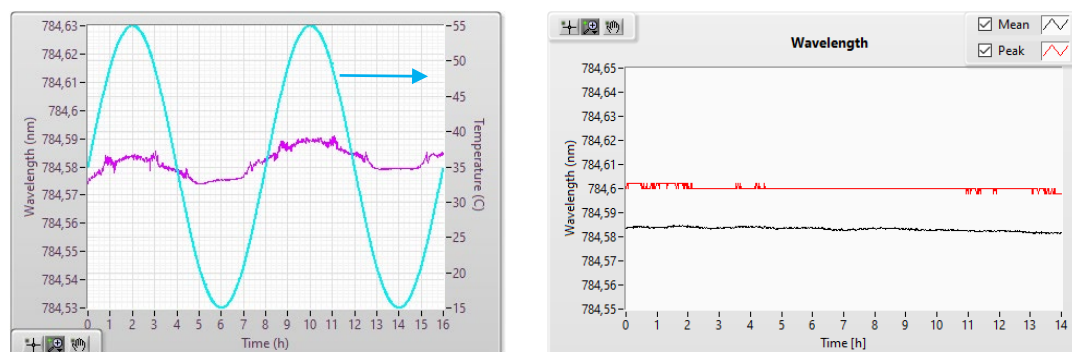


Figure 8. Measured wavelength drift during temperature cycling of the laser baseplate and at 35 °C constant temperature.

6. CONCLUSIONS

By introducing a novel design for frequency-locking semiconductor lasers using a single highly reflective VBG element and a polarization sensitive output coupler we were able to generate spectral performance for a 400 mW 785 nm that is normally only achievable using an additional external VBG clean-up filter. With an SMSR of >64 dB at +/- 300 pm and a linewidth of <27 pm the laser is well suited for low-frequency Raman applications. Assembly of the laser on a thermomechanically stable platform using high temperature adhesives for the optical components enabled demonstration of robust frequency-locking and stable spectral performance with low wavelength drift both over time and with varying baseplate temperatures.

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