Improving Raman spectroscopy with miniaturized diode lasers

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Portable, microbench light sources based on diode lasers emitting at two wavelengths improve the ratio of signal-to-background noise for chemical analysis without wavelength calibration.

Raman spectroscopy is a well-established method for material analysis, food safety control, and clinical diagnosis. Raman intensity depends on light frequency to the power of 4 ($I \propto \nu^4$), and thus excitation lasers produce higher signals in the visible range than in the near-IR range. For example, a visible-range excitation can lead to a strong fluorescence background that masks the relatively weak Raman signals of biological samples. It is possible to separate the Raman signals from high background noise using shifted-excitation Raman difference spectroscopy (SERDS), which requires a light source that alternates its emission between two fixed excitation wavelengths. Unfortunately, until now only bulky, complex, wavelength-switching laser systems have been available, and these require wavelength calibration.

Colleagues and I have developed light sources, based on diode lasers, that are suitable as excitation sources for SERDS. These lasers have a spectral width smaller than the spectral features under study (typically 10 cm$^{-1}$ for solid and liquid samples) and a highly stable peak wavelength (variation less than 1 cm$^{-1}$) that removes the need for calibration. Additionally, for SERDS two wavelengths are addressable with a distance of about 10 cm$^{-1}$. With these two excitation wavelengths, two Raman spectra (shifted by 10 cm$^{-1}$) are generated. The Raman lines can be separated from the background by calculating the difference between them.

Our first laser system uses two individually addressable semiconductor lasers as gain media (see Figure 1). The front facets of the devices have an anti-reflection coating that reduces reflection to 5%, and the rear facets are coated with an even more highly anti-reflection surface that reduces reflection to less than 5 x 10$^{-4}$. The light from the rear side is collimated with cylindrical micro-optics. We use two reflection Bragg gratings as wavelength-selective second resonator mirrors. The components sit on an aluminum nitride (AlN) micro-optical bench with a footprint of 20 x 5 mm. We combine the beams of the two laser cavities using a mirror and a beam splitter cube. In experiments, we mounted this subassembly on a conduction-cooled package with a footprint of only 25 x 25 mm. The device reaches an optical output power of up to 250 mW at the two selected wavelengths (671.0 and 671.6 nm) with a spectral distance of 13 cm$^{-1}$ for SERDS. The spectral width is smaller than 3 cm$^{-1}$ including 95% of laser intensity.

With this light source, we measured Raman spectra for ethanol alone and subsequently with added cresyl violet, a strongly fluorescent dye. Using SERDS, we were able to separate the Raman lines of ethanol from the fluorescent background. SERDS improved the signal-to-background ratio by a factor of 10.

In addition, we have developed monolithic dual-wavelength distributed Bragg reflector (DBR) diode lasers at 671 and 785 nm that are also suitable for SERDS. The devices have a footprint of 0.5 x 3 mm and are fabricated by single-step epitaxy. We designed and made two ridge waveguide sections with deeply

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etched surface DBR gratings with the necessary spectral spacing of \(10\text{cm}^{-1}\) in mind. We included a Y-branch coupler section in the semiconductor chip for one output section at the front facet. All sections can be individually controlled. We can achieve an output power of more than 100mW with a spectral width less than 0.5cm\(^{-1}\) and a spectral distance between the two emission lines of about 10cm\(^{-1}\), as desired.

Figure 2 shows the third light source we developed, which is based on generating at 488nm the second harmonic of a 976nm distributed feedback laser, using a periodically poled lithium niobate waveguide crystal. The two light beams have similar dependence of wavelength on temperature of about 0.07nm/K. We mounted this ‘second harmonic generation (SHG) microsystem light source’ on a 25\times5mm AlN microbench. By changing the temperature of the laser module the wavelength tunes with a coefficient of 37pm/K. An 8K temperature change shifts the wavelength shift by 0.3nm, that is, the wavenumber by 13cm\(^{-1}\), which is suitable for our SERDS experiments.\(^3\)

We used tartrazine (E102), an artificial food colorant solved in distilled water, as a test sample for SERDS measurements with the SHG microsystem light source. Resonance effects enhanced the Raman signal when we excited the sample at 488nm. Nevertheless, at low concentrations, the resonance Raman lines were hidden by a background signal. By exciting the sample with the two wavelengths alternately, we could use ‘shifted excitation resonance Raman difference spectroscopy’ (SERRDS). Using SERRDS as a contactless method, we found the E102 detection limit was in the range of 200 parts per billion, which is clearly below the limit of 100mg/l allowed in the European Union.\(^4,5\)

In summary, we have shown that diode-laser-based microsystem dual-wavelength light sources are capable of improving Raman spectroscopy by increasing the ratio of signal to background noise, especially when using SERDS in a fluorescent environment. We are now working to develop excitation lasers further by implementing the dual wavelength feature into a semiconductor laser chip.\(^6\)

### Author Information

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Bernd Sumpf received his diploma in physics in 1981 and a PhD in 1987 from the Humboldt University at Berlin, Germany. From 1993 till 1997, he worked at the Technical University Berlin, Germany, on high-resolution spectroscopy and difference frequency. In 2000 he joined FBH, where he works on high-brightness diode lasers and lasers for Raman spectroscopy.

Martin Maiwald received his diploma in physics in 2004 and a PhD in 2009 from the Technische Universität Berlin, Germany. His doctoral research was related to the development of diode-laser-based microsystem light sources for Raman spectroscopy. His current research area at FBH is in the field of diode lasers, non-linear optics for frequency conversion, and the development of compact diode laser systems for Raman spectroscopy.

### References

5. Further information on regulation 94/36EG. http://ec.europa.eu/food/fs/sfp/addit_flavor/flav08_en.pdf

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**Figure 2.** Second harmonic generation microsystem light source. (Reprinted with permission from FBH/schurian.com.)